STRUCTURAL AND SPECTROSCOPIC STUDIES WITH DITHIZONE AND ITS DERIVATIVES

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by

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Most of all I want to thank my parents for their understanding and encouragement; this work is dedicated to them both.

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CONTENTS

SUMMARY

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An *X*-ray crystal structure determination of 3-nitro-1,5-di(2,6-dimethylphenyl)formazan, ArN:N·C(NO_2):N·NHAr (Ar = 2,6-dimethylphenyl), has shown that the N-N-C-N-N chain is stabilized by an unusual hydrogen bond in the closed-ring *syn*,s-*cis* configuration relative to the formal double C=N and single C-N bonds. The bond lengths reveal complete π-electron delocalization along the chain which results in a mesomeric structure; the possibility of such a mesomeric structure existing in solution rather than a rapid tautomeric equilibrium between two limiting forms of the resonance hybrid has been considered in the light of i.r. and n.m.r. spectroscopic measurements.

The temporal changes in the visible absorption spectrum of *S*-methyldithizone, PhN:N·C(SCH_3):N·NHPh, have been shown to arise from *syn-anti* isomerization about the formal C=N double bond and rotation about the C-N single bond by considering the evidence provided by i.r. and n.m.r. spectroscopic studies combined with the *X*-ray crystal structure of the di(*o*-tolyl) homologue.

The parent compound dithizone, PhN:N·C(SH):N·NHPh, previously thought to exist as an equilibrium of thiol and thione forms in solution has now been shown to consist of a single species in solution mainly by consideration of its n.m.r. spectroscopic properties.

Organomercury(II) complexes of dithizone have been shown to be photochromic in solution; *X*-ray crystal structure determinations of phenyl- and methylmercury(II) dithizonate, besides revealing rare three-coordination of mercury, have been combined with spectroscopic measurements on the normal and activated forms to reveal the structure of the labile photo-isomers.

CHAPTER I

GENERAL INTRODUCTION

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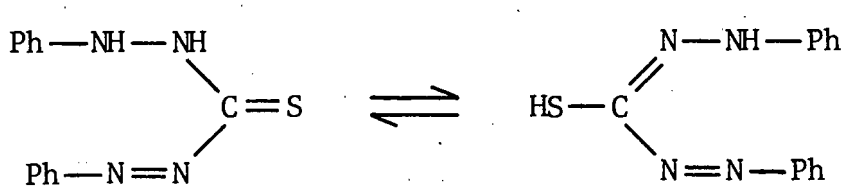
Dithizone (1a, 1b; H_2Dz) or 1,5-diphenylthiocarbazone [often called 3-thio(or mercapto)-1,5-diphenylformazan and also known as 3-thioxo-1,5-diphenylformazan or in *Chemical Abstracts* as diazene-carbothioic acid, phenyl-, 2-phenylhydrazide or phenylazothioformic acid 2-phenylhydrazide] was first synthesized in 1878 by Emil Fischer[1] during his investigation of the series of compounds resulting from the reactions of phenylhydrazine with carbon disulphide. With Besthorn[2] he also noted its reaction with certain heavy metals to form brilliantly coloured compounds. Some years later Bamberger *et al.*[3] prepared dithizone by a different route and reported the synthesis of a few of its metal complexes. However, it was not until 1925 that Helmuth Fischer[4] showed its great potential for the detection and determination of many heavy metal ions. It has now become more or less indispensible in trace metal analysis and there is an extensive literature concerning dithizone and its analytical applications. Irving[5,6] has very recently (1977, 1980) reviewed the whole subject.



(1a) Thione form

(1b) Thiol form

Dithizone is a violet-black solid, very sparingly soluble in water and exhibiting low solubility in most organic solvents to give strongly coloured solutions characterized by two intense absorption bands in the visible spectrum at *ca.* 450 and 620 nm (Figure 1). The presence of these two widely separated peaks gave rise to the hypothesis[7] that in organic solvents dithizone exists as a tautomeric equilibrium mixture of the thione (1a) and the thiol (1b) forms, one of which would give rise to the peak at *ca.* 450, the other to the peak at *ca.* 620 nm.

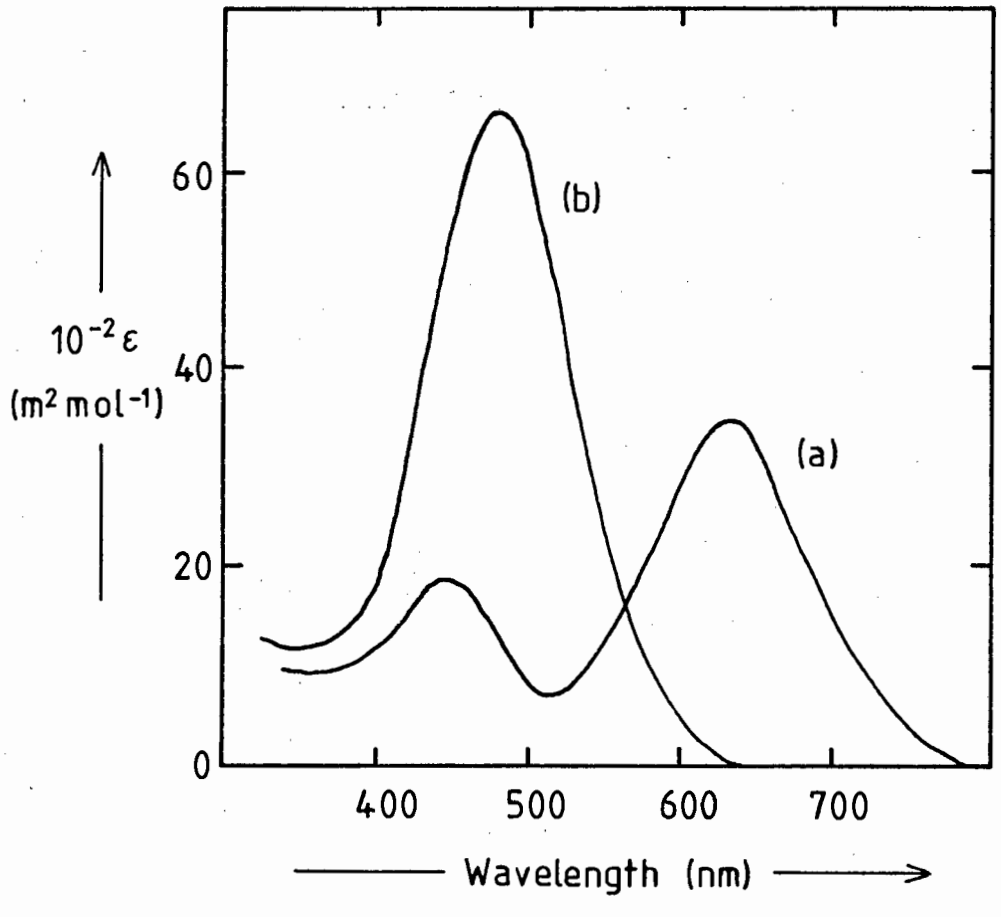
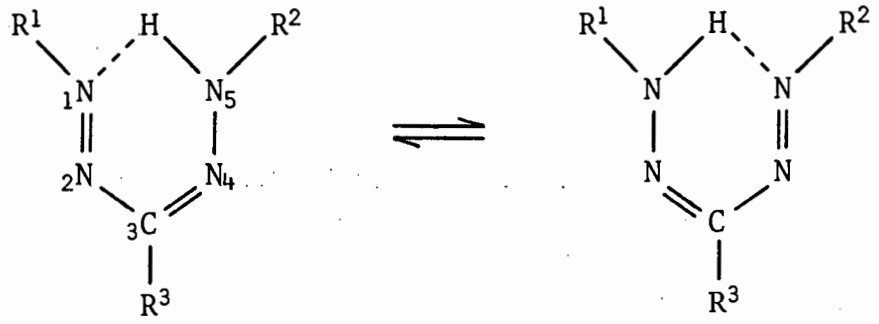


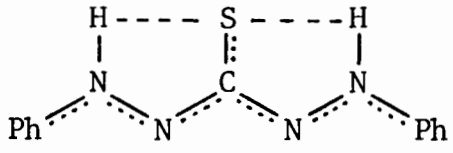
FIGURE 1 : Absorption spectra of (a) dithizone, H_2Dz, in CCl_4; (b) a typical metal dithizonate, $Hg(HDz)_2$, in CCl_4.

The tautomerism indicated by (1a) ⇌ (1b) must, however, be regarded as an oversimplification[5] since possible *cis-trans* isomerism about the azo-bond, -N=N-, and *syn-anti* isomerism about the :C=N- double bond increases the number of possible conformers, in addition to which tautomerism and internal hydrogen bonding in the formazans [(2a) ⇌ (2b)] has long been postulated[8] and should also be considered. The resolution of these problems [*e.g.*, by nuclear magnetic resonance (n.m.r.) studies] has recently been reviewed,[9] but no conclusive solution has thus far been reached.



(2a) (2b)

The solid state structure of dithizone (1c) has recently been determined by *X*-ray crystallography.[10] Dithizone crystallizes in the monoclinic space group $P2_1/n$ with a = 4.70(1), b = 22.53(3), c = 11.95(2) Å, and β = 82.0(3)°. The molecule (1c) is nearly planar, and of symmetry *mm* (C_{2v}) with the N-N-C-N-N chain extended and the C-S bond lying on the intersection of the mirror planes. The phenyl groups are twisted slightly out of the mean plane in opposite senses. It is



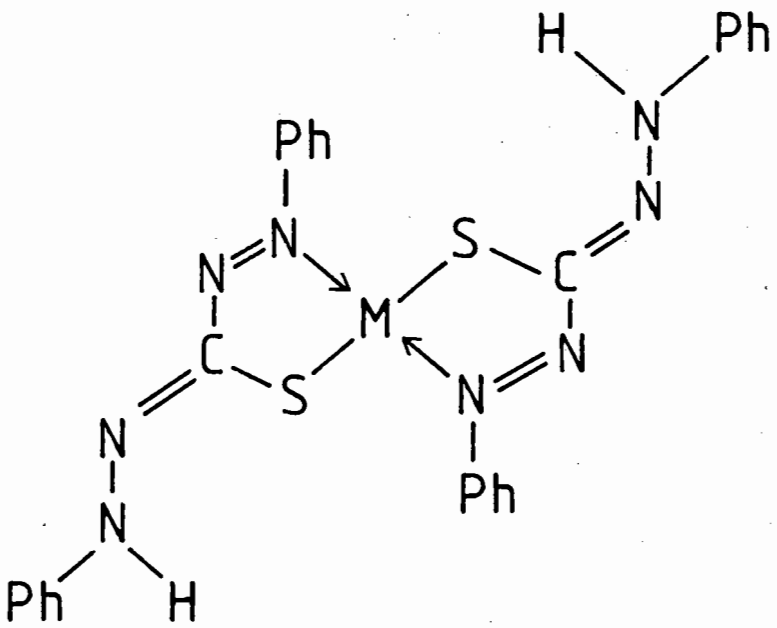
(1c)

evident from the measured bond lengths that π-electrons in the N-N-C-N-N chain are delocalized throughout and that there are no localized single or double bonds. The two imino hydrogen atoms are located as shown in (1c); both are weakly hydrogen-bonded to the sulphur atom.

When a solution of dithizone (H_2Dz) in carbon tetrachloride or chloroform is shaken with an aqueous solution of certain metallic[11] or organometallic[12] ions, dithizone behaves as a weak monobasic acid[13-15] of pK ~4.5 and forms strongly coloured complexes which are extracted into the organic phase. The solutions of metal dithizonates are characterized by a single intense absorption band in the visible spectrum located between 430 and 550 nm (Figure 1).

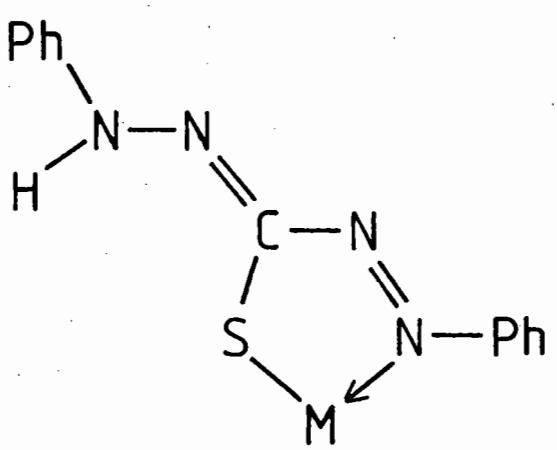
Although dithizone is an extremely sensitive reagent, it is not specific since it forms complexes (bonding through nitrogen and sulphur, Figure 2) with a variety of cations derived from metals grouped in the centre of the Periodic Table (see Table 1). Many complexes of organometallic cations such as $C_6H_5Hg^+$, $(CH_3)_2Tl^+$, and $(C_2H_5)_3Pb^+$ are also known.[16] However, when used in liquid-liquid extraction procedures, this reagent can be made more selective by a suitable adjustment of the pH of the aqueous phase or by the use of the appropriate masking agents to produce competitive complex formation in the aqueous phase.

As an analytical reagent dithizone suffers from certain disadvantages. It is difficult to obtain absolutely pure in the solid state and its solutions in organic solvents tend to deteriorate on keeping, especially in the presence of alkalis, oxidizing agents, and light. The actual causes of the deterioration of dithizone solutions have never been clearly defined, but it is generally regarded as an oxidation process probably catalysed by light.[17]



M = Ni^{2+}, Cu^{2+}, Pt^{2+}, Pd^{2+} (Square-planar)

M = Zn^{2+}, Hg^{2+} (Tetrahedral)



M = Ag^{+}, Cu^{+}, $(CH_3)_3Pb^{+}$, $(CH_3)_2Tl^{+}$, RHg^{+} (R = alkyl or aryl)

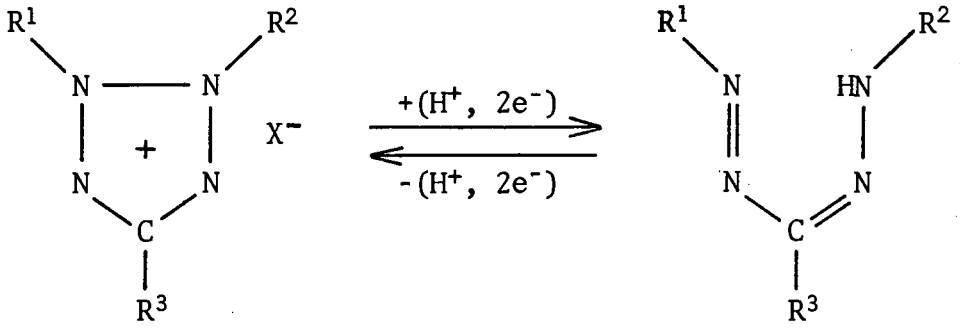
FIGURE 2 : Some modes of coordination of dithizone to metallic cations.

TABLE 1 : METALS FORMING COMPLEXES WITH DITHIZONE[a]

Mn	Fe	Co	Ni	Cu	Zn	-	-	-	Se
-	-	-	Pd	Ag	Cd	In	Sn	-	Te
-	-	-	Pt	Au	Hg	Tl	Pb	Bi	Po

[a] These metals can be extracted by dithizone from aqueous solution. Some metals (*e.g.* Fe, Cu, Hg) form different dithizone complexes according to their oxidation state. The situation with Se is still under discussion. In addition, the lanthanons give complexes of low stability in 50% aqueous ethanol, and several other metals may form dithizonates in the absence of water and at high ligand concentration.[5]

One of the main areas of concern in this work has been the elucidation of the structure of dithizone in solution. The primary bonding characteristics are known from the recently published crystal structure,[10] but the actual sterochemistry of dithizone in solution is still a matter of conjecture despite the voluminous literature[5,6,11] on the synthesis, applications, and spectral characteristics of the parent compound, its substituted analogues, and its metal complexes. Since dithizone is formally a 3-thioformazan (1b) familiarity with the structural problems posed by the parent formazan ring system (2) must be considered in addition to the additional features introduced by the possibility of thiol-thione tautomerism. The formazans[18] find wide application in biological chemistry, principally as colorimetric reagents for the detection of enzymatic oxidation-reduction reactions. This is due to the ability of the colourless tetrazolium molecule [as (3)] to accept electrons from one or more intermediates in the biological system and be reduced to the highly coloured formazan (2).

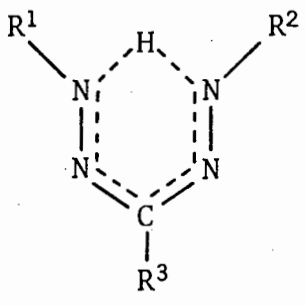


(3) (2)

Tetrazolium salt Formazan

The reverse reaction, *viz.* oxidation of the highly coloured 3-carboxymethylthio-1,5-diphenylformazan [(2); $R^1 = R^2 = Ph$, $R^3 = SCH_2CO_2H$] to the colourless tetrazolium salt [(3); $R^1 = R^2 = Ph$, $R^3 = SCH_2CO_2H$], has recently been adapted to a sensitive and selective spectrophotometric method for the determination of Tl^{3+} and Au^{3+} in this laboratory.[19]

Early work on formazans[20-22] suggested that two isomers of structure (2a) or (2b) could be prepared if unlike substituents were attached to N(1) and N(5) of a formazan ring. Later work[23-26] indicated that internal hydrogen bonding rendered the isomers interconvertible and hence indistinguishable. Nineham,[8] in summarizing the early literature on this question, cited evidence which enabled him to state: 'When all three substituent groups in a molecule are alike only one formazan can be synthesized. When two of the three groups are the same only two isomers can be prepared; one with the odd group attached to carbon, the other with the odd group attached to nitrogen. When all three substituents are different, three isomers can be prepared'.[27] Hence the structure of the formazan ring in solution may be represented by a rapid tautomeric equilibrium between the two cyclic hydrogen-bridged structures (2a) $\rightleftharpoons$ (2b). This classical viewpoint has received support from infrared (i.r.) and n.m.r. spectral work (see Chapter II), but the possibility of a mesomeric structure [as (2c)] derived from a resonance hybrid of the limiting forms (2a) and (2b), as originally speculated by Kuhn and Jerchel[24] and Hunter and Roberts[26] in 1941, has

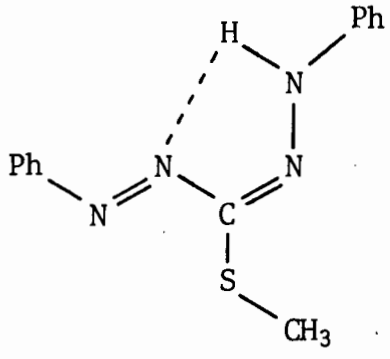


(2c)

not been excluded. This possibility is examined in Chapter II of this thesis, where it is shown by *X*-ray crystallography that 3-nitro-1,5-di(2,6-dimethylphenyl)formazan does indeed possess a mesomeric structure in the solid state [as (2c); $R^1 = R^2$ = 2,6-dimethylphenyl, $R^3 = NO_2$], and that this structure is common to a series of 3-nitro-1,5-diaryl-formazans. ^1H, ^{13}C, and ^{15}N n.m.r. and i.r. spectroscopy is used to investigate the possibility of a mesomeric structure in solution as well.

The classical method of determining the structure in potentially tautomeric systems such as dithizone [(1a) $\rightleftharpoons$ (1b)] is to compare the parent substance with derivatives in which the structure has been locked unambiguously by methylation into one or other of the possible tautomeric forms. This fails with dithizone,[28] for the absorption spectrum of *S*-methyldithizone [3-methylthio-1,5-diphenylformazan; (4)], in which the structure should be locked in the thiol form, does not possess a single band that could be correlated with the band of dithizone at either *ca.* 450 or *ca.* 620 nm. On the contrary, although a fresh solution of *S*-methyldithizone in, *e.g.*, chloroform is permanganate pink, with well-defined bands at 270 and 550 nm (ε_{550} = 1225 m^2 mol^{-1}), on standing in the dark at room temperature the colour changes to yellow, and the spectrum then shows bands at 280, 420, and 540 nm (ε_{420} = 1775 m^2 mol^{-1}), the band at 550 nm becoming less intense as the new band appears at 420 nm.[29] Analogous effects appear with many red formazans[30-33] which are converted to a yellow isomer on standing or on irradiation of solutions in appropriate solvents. *Cis-trans* isomerism about the -N=N- bond or *syn-anti* isomerism about the :C=N- bond is thought to be involved.[29-33] Concentration of solutions of *S*-methyl-

dithizone (whether in the pink *or* yellow form) deposits only the magenta-red solid, which has been shown crystallographically[34] to have the structure (4).



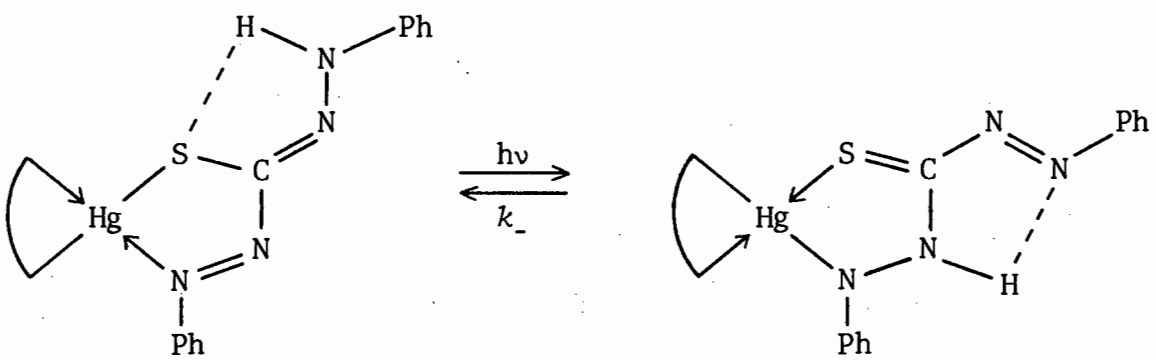
(4)

The chance discovery that 3-methylthio-1,5-di(*o*-tolyl)formazan gives the same two isomers in chloroform solution but crystallizes as the yellow isomer has enabled the structure of the yellow isomer to be determined by *X*-ray crystallography. This is reported in Chapter III, where in addition ^{1}H and ^{13}C n.m.r. and i.r. spectroscopic studies on a series of 3-methylthio-1,5-diarylformazans in solution are reported, which elucidate the structural changes which take place on isomerization of *S*-methyldithizone and its homologues. The results of this study, combined with those of Chapter II, are then applied to the red $\rightleftharpoons$ yellow isomerism so widely found in the formazan group.

The structure of the parent compound dithizone itself is considered in Chapter IV, chiefly in the light of the ^{1}H and ^{13}C n.m.r. spectra of dithizone, its analogues, and its derivatives. Use has also been made of ^{15}N-enriched dithizone and some effort was put into perfecting methods for the small-scale synthesis of ^{13}C- and ^{15}N-enriched material.

The selenium analogue of dithizone, 'selenazone' or 3-seleno-1,5-diphenylformazan,[35] was synthesized in an attempt to observe by n.m.r. the little-studied ^{77}Se nucleus. The combined results of this study along with those of Chapters II and III are then used to establish the structure of dithizone in solution with reasonable certainty, and to the exclusion of a thiol-thione equilibrium.

While studying the use of dithizone in the determination of traces of mercury, Irving, Andrew, and Risdon[36] were surprised to see an orange-yellow chloroform solution of mercury(II) bis(dithizonate) [$Hg(HDz)_2$, (5a); the conformation of only one of the dithizone residues is shown in detail] change in colour to an intense royal blue upon accidental exposure to the year's first spell of sunshine in March 1946.[37] The yellow coloration returned slowly in diffuse daylight or in the dark, and immediately on shaking with a solution of mercury(II) chloride in dilute sulphuric acid. Upon exposure to direct sunlight the blue coloration developed again, and the sequence of colour changes could be repeated at will.[36] It was later discovered that Reith and Gerritsma had made the same observation a year earlier,[38] and these workers noted that the photochromic effect was inhibited by the presence of dilute acetic acid.

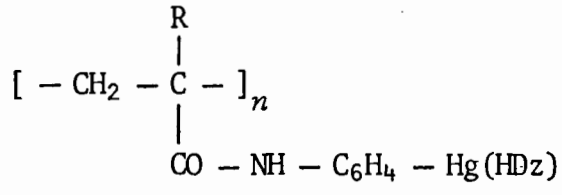


(5a) yellow (5b) blue

This photochromic effect was rediscovered 5 years later by Webb, Bhatia, Corwin, and Sharp,[39] but the curious phenomenon was not followed up in depth until 1965 when the American Cyanamid Company recognized its potential use in solar batteries, car windscreens, and sunglasses. Thus Meriwether, Breitner, and Sloan[40] found this reversible photochromism to be a general reaction of all metal dithizonates, but the reverse reaction is generally too rapid to allow visual observation of a colour change. The long half-life (of the order of minutes) of the blue form in the mercury complex, however, allows investigation of this phenomenon by conventional techniques. Meriwether's group then investigated the environmental factors influencing the colour change, observed the kinetics of the reversion reaction, and obtained the i.r. spectrum of the blue form.[41] Their results enabled them to suggest structure (5b) for the blue form and they also proposed a mechanism for the isomerization involving a shift of the hydrogen atom from the 5-nitrogen to the 2-nitrogen of the dithizonate moiety and a redistribution of electrons to yield a thiocarbonyl group in the blue form. An *X*-ray crystal structure of $Hg(HDz)_2 \cdot 2$(pyridine) by Harding[42] in 1958 had established a rather distorted tetrahedral coordination with the bonding characteristics shown in structure (5a). Alsop repeated this structure determination in 1971 using better intensity data.[43] More recently (1978) kinetic studies[44] were reported using continuous photolysis and flash photolysis techniques on a variety of metal dithizonates, but no mention was made of possible structures for the yellow and blue forms.

The photochromic effect persists when the grouping -Hg(HDz) forms part of most organic structures, and a very large number of patents have

been taken out for, *e.g.*, photochromic dyes for fabrics which then change colour (reversibly) in sunlight from yellow to blue,[45-47] for incorporation into resins and plastics to form photochromic films, glasses, or lenses,[48-50] and even as integral parts of photochromic polymers which may be represented[51,52] as (6) and (7). An intriguing



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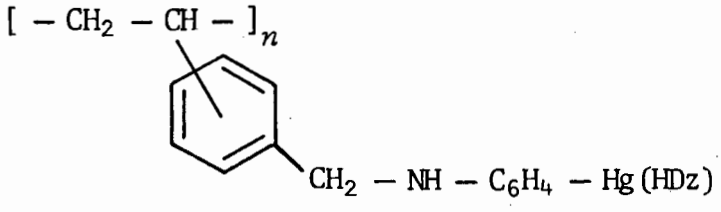


(7)

study[53] was made under contract for the United States Army on photochromic colorants potentially useful for a 'chameleon' type camouflage system for military uniforms.

Mercury(II) bis(dithizonate) is insoluble in water and barely soluble in the common organic solvents, forming a saturated solution in carbon tetrachloride at approximately 10^{-3} *M*. This insolubility complicates

the study of the photochemistry of the system by i.r. and n.m.r. techniques and offsets the advantages gained from the extensive half-life of the irradiation-induced blue form. Chapter V of this thesis reports how the limitations imposed by the insolubility of $Hg(HDz)_2$ were overcome when a series of organomercury(II) mono(dithizonates), RHg(HDz), was synthesized in the hope that the less symmetrical and lower molecular weight compounds would retain the photochemical properties of the bis-dithizonate yet prove amenable to i.r. and particularly n.m.r. investigation. The 1 : 1 organomercury(II) complexes were also made from several derivatives of dithizone substituted by methyl groups at various positions on the phenyl rings in order to enable conformational changes to be monitored by ^1H n.m.r. spectroscopy.

It has not proved possible to secure crystals of the blue form of any of these organomercury(II) dithizonates, even by carefully and slowly concentrating solutions kept in the blue form by constant and intense illumination : only the stable yellow form crystallizes out. Whereas it has only been possible to infer the structure of the blue isomeric form of these compounds from spectroscopic measurements on irradiated solutions, the structure of the yellow form has been established unambiguously by *X*-ray crystallographic studies on phenylmercury(II) dithizonate and methylmercury(II) dithizonate. These are also reported in Chapter V. Since dithizone is a bidentate chelating agent the interesting possibility of three-coordination about the mercury atom arises in these 1 : 1 dithizonates derived from organomercury(II).

CHAPTER II

MESOMERISM IN 3-NITRO-1,5-DIARYLFORMAZANS

CHAPTER II

MESOMERISM IN 3-NITRO-1,5-DIARYLFORMAZANS

1. Introduction

Some properties of formazans

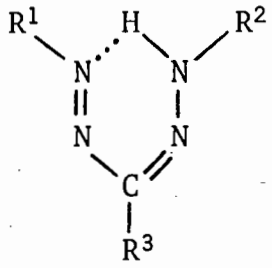
Formazans in general (2) are solids of relatively low melting point for the size of the molecules; for example, most triarylformazans tend to melt in the range 150-215°C. They are characterized by intense colours ($\varepsilon > 10^3$ m^2 mol^{-1}), ranging from yellow through shades of red to a deep purplish black. At the same time, many show brilliant reflex colours and their appearance is often very striking. The influence of substituents on the colour follows rules familiar in the dyestuffs field;[8] the effect of nitro-groups substituted in the benzene rings has been described in detail.[54] Formazans with aliphatic substituents (hydrogen, methyl, carboxyl, *etc.*) attached to the 3-carbon atom have lighter colours and a greater solubility in common organic solvents than have the aryl derivatives. Triarylformazans are often particularly soluble in chloroform and acetone; in water the solubility appears to be negligible, the solvent being scarcely coloured. As the molecule is loaded with larger groups such as diphenyl or phenylazo, the colour of the crystals becomes almost black and the solubility very low; some biformazans of high molecular mass seem to have no appreciable solubility in any solvent but nitrobenzene.[18] The only water-soluble formazans are those in which specifically solubilizing groups have been introduced into the molecule. Formazans behave both as very weak acids and as weak bases; [28,55-58] both types of salt

which can result are hydrolyzed by water in the cold. Formazans substituted with specific acidic or basic groups show the behaviour characteristic of these groups.[59] Formazans generally form metal complexes, particularly with copper, nickel, cobalt, palladium, and silver. Some of these have been studied in detail[55,60-68] and their properties adduced as evidence for a chelated hydrogen-bridged ring structure for the formazans themselves.

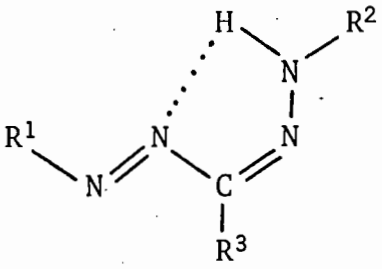
Isomerism in formazans

As intimated in Chapter I, all formazans can exist in a number of forms owing to isomerization about the :C=N- and -N=N- double bonds. Additional structures could arise from rotation about single bonds, and structures (2a), (2d) - (2j) illustrate the several possible stereoisomers which should be considered in discussing the structures of formazans.

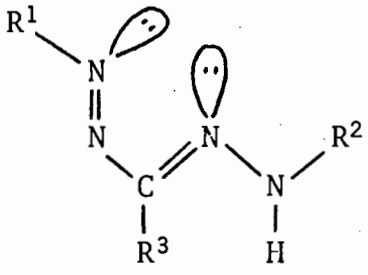
The configuration about the :C=N- bond is designated *syn* with the anilino and phenylazo groups on the same side of the double bond [(2a), (2d), (2g), (2h)].[30,31,69] If these groups are on opposite sides of the double bond they are designated as *anti* [(2e), (2f), (2i), (2j)]. *Cis-trans* isomers are possible about the -N=N- double bond, although serious steric crowding would appear to make isomers with *cis*-configurations unlikely and in general only the *trans*-isomers [(2a), (2d), (2e), (2f)] need be considered.[59] The C-N single bond linking the phenylazo-group to the 3-carbon atom is similar to the central bond in buta-1,3-diene and the various forms can be further distinguished as s-*cis* [(2a), (2e), (2g), (2i)] or s-*trans* [(2d), (2f), (2h), (2j)] isomers.[70,71]



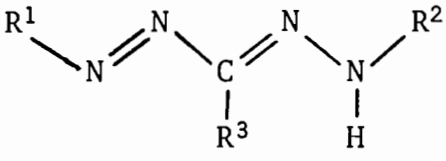
(2a) *syn*, s-*cis*, *trans*



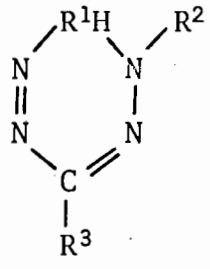
(2d) *syn*, s-*trans*, *trans*



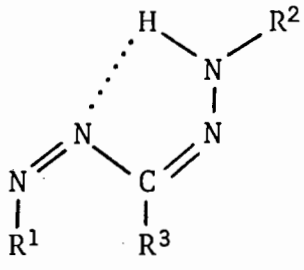
(2e) *anti*, s-*cis*, *trans*



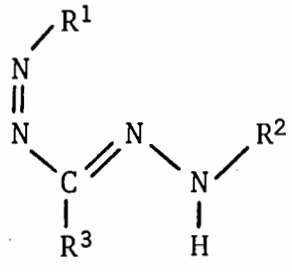
(2f) *anti*, s-*trans*, *trans*



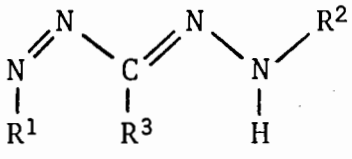
(2g) *syn*, s-*cis*, *cis*



(2h) *syn*, s-*trans*, *cis*



(2i) *anti*, s-*cis*, *cis*

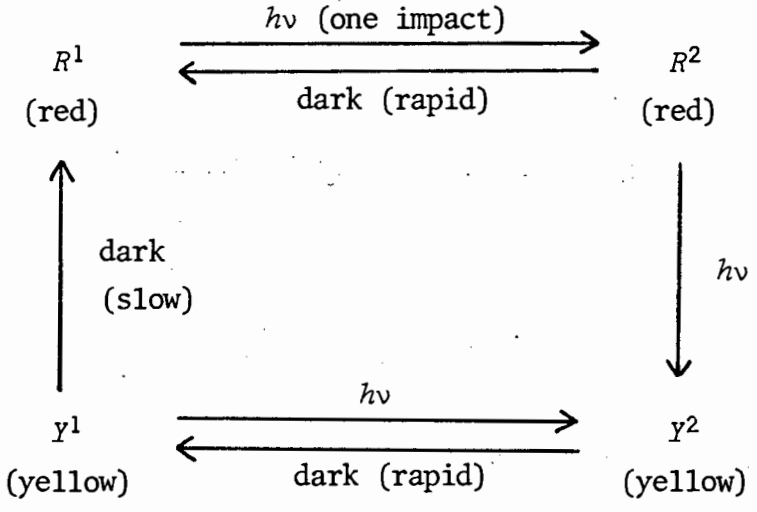


(2j) *anti*, s-*trans*, *cis*

The now familiar observation of the conversion of many red formazans to a yellow isomer on irradiation of solutions in appropriate solvents with visible light was first investigated by Hausser, Jerchel, and Kuhn in 1949.[30] They showed that the occurrence of two forms of a formazan, red and yellow, was, if not universal, at least of wide occurrence. Thus in the formazans of formula [(2); $R^1 = R^2 = Ph$, $R^3 = Me$] the solid is yellow and forms a yellow solution in methanol. When it is dissolved in benzene and kept in the dark, an equilibrium mixture of red and yellow forms is obtained. This was analyzed by measuring the absorption spectra. When R^3 is changed to n-heptyl, the solid is red, but gives a solution of the almost pure yellow form in ethanol, and an almost pure red form in benzene. The prediction that in an intermediate case, the two forms might be isolated in a pure state from different solvents was realized in the case where $R^3 = Et$. This formazan was obtained as orange needles, m.p. 102-103°C, from methanol, and as red needles, m.p. 73-75°C, from benzene. No exact assignation of structure to these two forms was attempted, but they interpreted their results in terms of the four possible geometrical isomers resulting from different orientations about the :C=N- and -N=N- double bonds, *viz* (2a), (2e), (2g), and (2i).

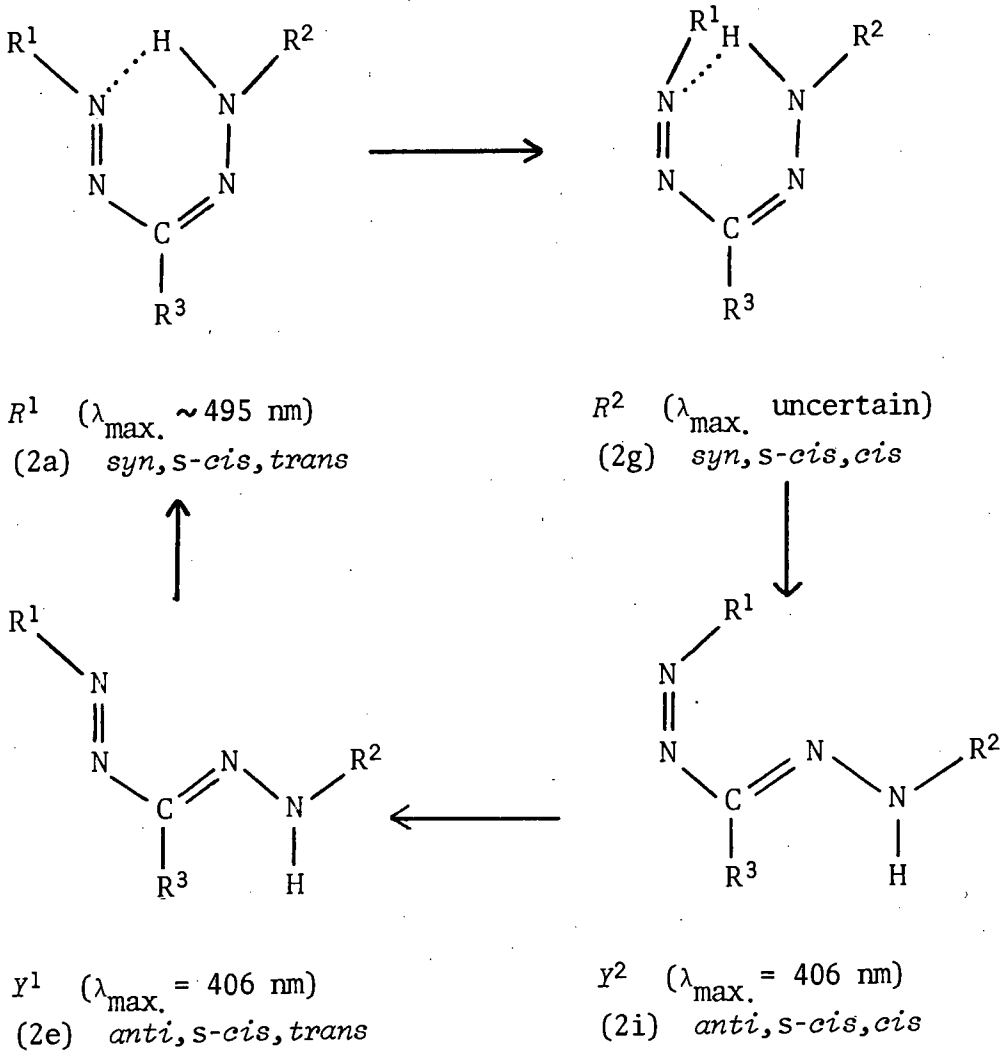
Hausser[72] then measured the quantum yields of the red $\rightleftharpoons$ yellow change in triphenylformazan [(2); $R^1 = R^2 = R^3 = Ph$] irradiated by light of wavelength 490 nm. His results showed that this change involved a photochemical intermediate which was reconverted to the red form with a half-life of 17 seconds. Such measurements showed a cycle of events involving two red and two yellow forms. The red form R^1,

stable in the solid state, is converted to a short-life red form R^2, which is converted by another quantum of light to the yellow form Y^2. This too, is of short life and rapidly passes in darkness to the more stable yellow form Y^1. This reverts to the R^1 form slowly in darkness, but catalysts influence the change strongly. The absorption spectra of the short-life intermediates R^2 and Y^2 show small differences from those of R^1 and Y^1, respectively. The changes observed were then summarized as follows:



Kuhn and Weitz[31] then, in 1953, discussed the precise allocation of these four experimentally observed forms to the theoretical structures mentioned above [(2a), (2e), (2g), (2i)]. They assumed that the observed changes were due to interconversions of the geometrical isomers, accompanied by opening or closing of the chelated hydrogen bridge (2a). By analogy with the changes in the light absorption of the different geometrical isomers of certain azo-compounds, they assigned the stable red form R^1 to the *syn*,s-*cis*,*trans* form (2a), and the unstable red form

R^2 to the *syn*,s-*cis*,*cis* form (2g). Thus the first change on illumination ($R^1 \rightarrow R^2$) involved a change of configuration about the -N=N- system from *trans* to *cis* without rupturing the hydrogen bridge. In the change to yellow ($R^2 \rightarrow Y^2$), the chelation is destroyed (together with the resonance in the molecule) when the :C=N- bond assumes an *anti*-configuration. Thus the yellow form Y^2 was said to be in the *anti*,-s-*cis*,*cis* form (2i), and the more stable yellow form Y^1 the *anti*,s-*cis*,-*trans* form (2e). The rapid dark reactions are *cis* → *trans* conversions and the slow dark reaction is an *anti* → *syn* change. The cyclic process in light was therefore rewritten in terms of isomeric structures as follows ($R^1 = R^2 = R^3 = Ph$):



R^1 ($\lambda_{max.}$ ~495 nm)
(2a) *syn*,s-*cis*,*trans*

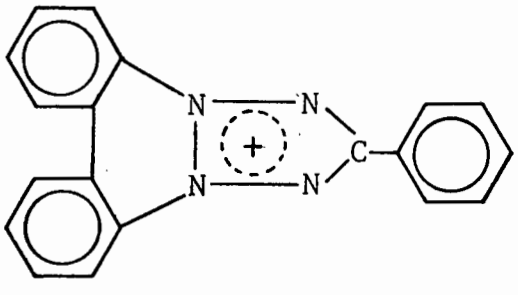
R^2 ($\lambda_{max.}$ uncertain)
(2g) *syn*,s-*cis*,*cis*

Y^1 ($\lambda_{max.}$ = 406 nm)
(2e) *anti*,s-*cis*,*trans*

Y^2 ($\lambda_{max.}$ = 406 nm)
(2i) *anti*,s-*cis*,*cis*

Since their formulation these hypotheses have remained unchallenged in spite of their speculative nature. By the end of Chapter III of this thesis it will be possible to confirm certain aspects of these theories and reject others; for the present, Nineham's 1955 review is quoted: 'In summing up, it now seems safe to say that, after many years of controversy, the general problem of isomerism in formazans has been clarified: only one form of the normal stable solid formazan is known, even when the two substituents attached to nitrogen are dissimilar; in solution, the absence or presence of light can give rise to two forms of considerable stability, one with a hydrogen bridge and one without. In addition, two transient forms may occur during the transformation'.[73]

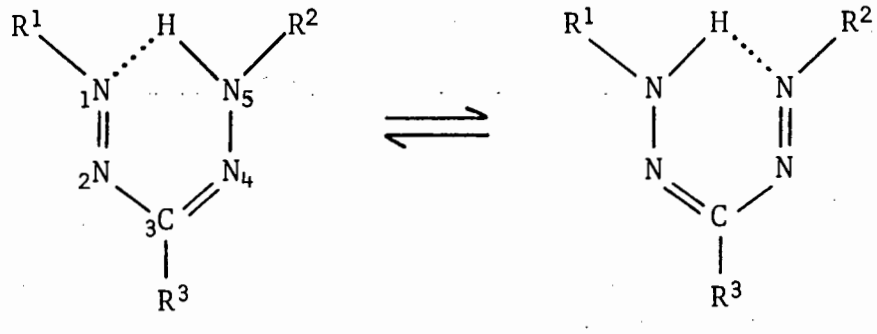
It is worth mentioning that the effect of ultraviolet (u.v.) light on formazans is quite different from that of visible light. In the case of triphenylformazan [(2); $R^1 = R^2 = R^3 = Ph$] auto-oxidation occurs, leading to the formation of the diphenylenetetrazolium salt (8), a compound which is also produced by the action of u.v. light on triphenyltetrazolium chloride [(3); $R^1 = R^2 = R^3 = Ph$, X = Cl].[72]



Cl^- (8)

Tautomerism in formazans

In addition to the problems of isomerism outlined above, there remains the question of tautomerism in the hydrogen-bridged *syn*,s-*cis*,*trans* formazans (2a). It was well established by 1955[8,23-26] that internal hydrogen bonding rendered indistinguishable the two hypothetical isomers having unlike substituents attached to N(1) and N(5). Hence the structure of the closed formazan ring in solution has invariably been represented by a rapid tautomeric equilibrium between the two equivalent structures (2a) $\rightleftharpoons$ (2b):

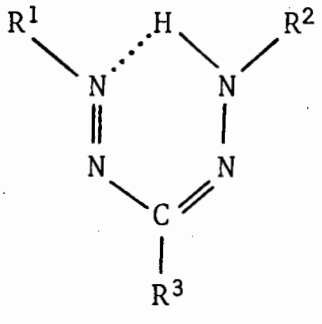


(2a) (2b)

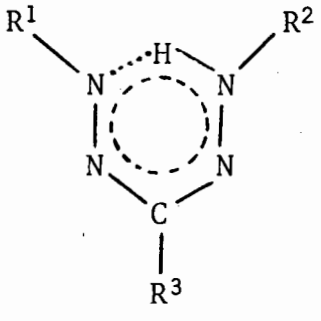
Most of the additional data to appear recently have been interpreted as confirming this classical viewpoint. The first ^{1}H n.m.r. spectral study showed that the observed equivalence of forms (2a) and (2b) required rapid tautomerization, with an estimated lower limit for the rate constant being *ca.* 10^3 s^{-1}.[74] The ^{15}N-H coupling constants in the ^{1}H n.m.r. spectra of ^{15}N-enriched 1,3,5-triphenylformazan [(2); $R^1 = R^2 = R^3 = Ph$],[75] the sugar formazan 3-(penta-*O*-acetyl-D-galactose)-1,5-diphenylformazan [(2); $R^1 = R^2 = Ph$, $R^3 = (CHOAc)_4$•-

CH_2OAc],[76] and more recently 3-carboxymethylthio-1,5-diphenylformazan and its methyl ester [(2); $R^1 = R^2 = Ph$, $R^3 = SCH_2CO_2H$ or SCH_2CO_2Me],[77] have been interpreted in terms of a fast intramolecular proton exchange between the terminal nitrogen atoms with respect to the n.m.r. time-scale.

I.r. spectral work has resulted largely in band assignments with interpretations also favouring the rapid tautomeric equilibrium (2a) $\rightleftharpoons$ (2b).[32,33,78,79] However, Schiele and co-workers[80-83] maintain that, in certain cases at least, the formazans are more truly represented by a hybrid involving structures (2a) and (2k) than the classical viewpoint of (2a) $\rightleftharpoons$ (2b).



(2a)



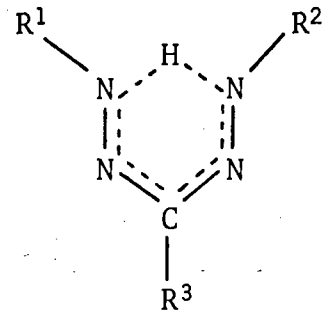
(2k)

Their conclusions are based on i.r. spectral evidence which is interpreted as showing that the ring system has an asymmetrical distribution of electron density. In Schiele's model the R^3 aryl-group and the 'quasi-aromatic'heterocycle(a term which will be carefully considered later in this Chapter) are largely coplanar, but the hydrogen bridge as well as the R^1 and R^2 substituents show a departure from coplanarity,

the extent of which is said to depend on the electron-withdrawing or electron-attracting nature of the substituent in the R^3 aryl-group.

3-Nitro-1,5-diarylformazans

All these studies, however, do not exclude the possibility of a mesomeric formazan ring [as (2c)] derived from a resonance hybrid of the limiting



(2c)

forms (2a) and (2b), as originally speculated in early studies.[24,26] Since the 3-nitro-1,5-diarylformazans [(2); $R^1 = R^2 = Ar$, $R^3 = NO_2$] are prepared as precursors in Bamberger's[3] synthetic route to the corresponding dithizones (see Chapter IV), the opportunity was taken to examine a series of nitroformazans in the hope of clarifying the nature of the cyclic hydrogen-bridged ring in the red *syn,s-cis,trans* formazans. The nitroformazans studied (Table 2) were particularly suitable for this purpose since they crystallized as red solids and showed no presence of the yellow isomer in benzene, chloroform, or acetone solutions even after intense irradiation with visible light. In addition, it was expected that the presence of methyl substituents on the phenyl rings (Table 2) would facilitate the study of the red nitroformazans in

TABLE 2 : SYMMETRICAL 3-NITRO-1,5-DIARYLFORMAZANS SYNTHESIZED IN THIS WORK

Number	Aryl group
(9)	phenyl
(10)	*p*-tolyl
(11)	*m*-tolyl
(12)	*o*-tolyl
(13)	3,5-dimethylphenyl
(14)	2,6-dimethylphenyl
(15)	2,4,6-trimethylphenyl
(16)	*p*-isopropylphenyl
(17)	*p*-n-butylphenyl

solution by ^1H n.m.r. spectroscopy. 3-Nitroformazans as a whole have not received much attention, but reports do exist on, *e.g.* their synthesis,[84] physical properties,[58] and metal complexes.[67]

Preparative work

The nitroformazans (9) - (17) were prepared[3,67,84-86] (see experimental section of this Chapter) by coupling the corresponding diazotised arylamines with nitromethane at -5°C:

$$2ArN_2^+Cl^- + CH_3NO_2 \rightarrow Ar.N{:}N.C(NO_2){:}N.NH.Ar + 2HCl \qquad (i)$$

Satisfactory yields were obtained (20-60%) except in the case of nitroformazans (14) and (15) where there are methyl groups in both the 2- and 6-positions on the phenyl rings. The average yield of (14) and (15) in several attempted preparations was about 1%, and this could not be improved by lowering the reaction temperature to -20°C, by altering the concentration of reagents, or by carrying out the diazotisation in sulphuric rather than hydrochloric acid. Using Hodgson's[87,88] general diazotisation procedure in a concentrated sulphuric and glacial acetic acid mixture and actually isolating the solid diazonium sulphates gave good yields of the solid salts. However, when these salts were redissolved in an aqueous buffer and mixed with an alkaline nitromethane solution under the usual conditions required for coupling, no coupling reaction occurred. It is tempting to attribute the impracticably small yields obtained for (14) and (15) to steric hindrance to the formation of the diazonium salt by the methyl groups in the 2- and 6-positions on the benzene rings; however, the coupling reaction itself is clearly the limiting step. The fact that the corresponding arylmercury(II) chlorides

were synthesized[89] [as equation (ii)] in good yield (Chapter V) from

$$ArN_2^+Cl^- + HgCl_2 + Cu_2Cl_2 \longrightarrow ArHgCl + 2CuCl_2 + N_2 \qquad \text{(ii)}$$

the diazonium salts of 2,6-dimethylaniline and 2,4,6-trimethylaniline also points to this conclusion, as does the synthesis[90] (Chapter IV) of 2,6-dimethylphenylhydrazine from the diazonium salt of 2,6-dimethylaniline:

$$ArN_2^+Cl^- \xrightarrow[(Na_2SO_3,\ H_2O)]{+4e^-,\ +4H^+} Ar.NH.NH_3^+Cl^- \xrightarrow{OH^-} Ar.NH.NH_2 \qquad \text{(iii)}$$

A steric effect is not expected at the coupling stage since the reaction sites are then fairly remote from the methyl groups on the phenyl rings. A search of the literature revealed no special mention of diazo-coupling of 2,6-disubstituted arylamines, and no satisfactory explanation has been found to account for the almost negligible yields of (14) and (15).

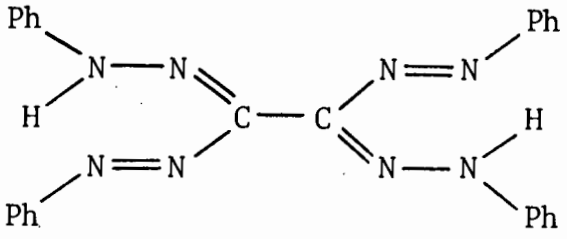
Once again as precursor to the corresponding dithizone, the nitroformazan (9) was synthesized from 96 atom-% ^{15}N-enriched aniline to give the nitroformazan labelled at N(1) and N(5) with ^{15}N. The nitroformazan (9) labelled with ^{13}C at C(3) was synthesized from 91 atom-% ^{13}C-enriched nitromethane. Several scaled-down 'dummy runs' were done in order to optimize reaction conditions before attempting the small-scale synthesis of the labelled formazans from their very expensive isotopically enriched starting materials. Details are recorded in the experimental section of this Chapter.

X-Ray crystal structures of formazans

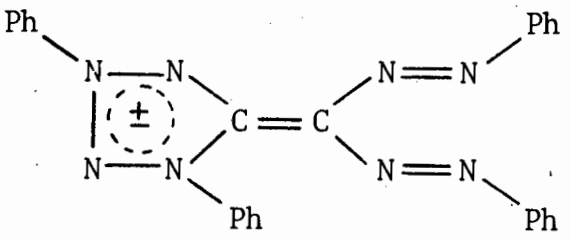
X-Ray crystallographic investigations of formazans have yielded examples of the *anti,s-trans* configuration relative to the formal double C=N and

single C-N bonds [as(2f)] in 1,5-diphenylformazan [(2f); $R^1 = R^2 = Ph$, $R^3 = H$],[91] 3-thio-1,5-diphenylformazan (dithizone) [(2f); $R^1 = R^2 = Ph$, $R^3 = SH$],[10] 3-isopropylthio-1,5-diphenylformazan [(2f); $R^1 = R^2 = Ph$, $R^3 = CH(CH_3)_2$],[92] and 3-methylthio-1,5-di(*o*-tolyl)formazan [(2f); $R^1 = R^2 =$ *o*-tolyl, $R^3 = SCH_3$] (reported in Chapter III of this thesis),[93,94] as well as examples of the *syn,*s-*trans* configuration [as(2d)] in 3-methylthio-1,5-diphenylformazan [(2d); $R^1 = R^2 = Ph$, $R^3 = SCH_3$],[34] and 3-carboxymethylthio-1,5-diphenylformazan [(2d); $R^1 = R^2 = Ph$, $R^3 = SCH_2CO_2H$],[95,96] but until recently no instance of the closed ring *syn,*s-*cis* isomer (2a) had been reported, although this configuration is adopted when 3-methyl-1-(or 5)-phenyl-5(or 1)-*p*-tolylformazan deprotonates to form the bis-chelate with Ni(II) by coordination through N(1) and N(5),[97] when 1-(2-hydroxyphenyl)-3,5-diphenylformazan acts as a terdentate ligand to complex with Cu(II) or Ni(II) through N(1), N(5), and O (the fourth coordination site being satisfied by NH_3),[98] and when 1,5-diphenylformazan coordinates through N(1) and N(4) as a non-ionized ligand to form a bis-chelated Cu(I) cation.[99]

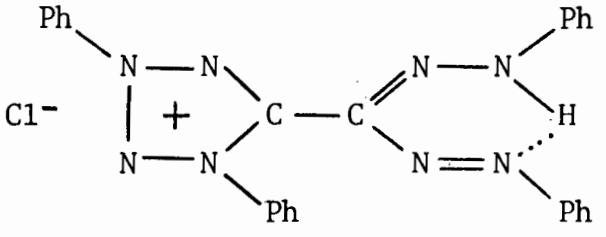
While work on this thesis was in progress, however, the structure of 'diformazyl', which had been formulated as 1,1′,5,5′-tetraphenyl-3,3′-biformazan (18a), was shown to be 5-[bis(phenylazo)methylene]-1,3-diphenyltetrazoline betaine [(18b) and canonical forms] based on the *X*-ray structure analysis of the hydrochloride and on degradation reactions of the base.[100] The hydrochloride adopts a closed ring *syn,*s-*cis* structure (19) and provides the first crystallographic evidence for this configuration in uncoordinated formazans.



(18a)



(18b)



(19)

The nitroformazans (14) and (15) were, as described above, obtained in extremely low yield. However, after chromatographic purification and recrystallization a few large needles of 3-nitro-1,5-di(2,6-dimethylphenyl)formazan (14) were obtained, and a full *X*-ray structural analysis was undertaken in the hope that an explanation for the difficulty in synthesis might be found in some structural feature of the molecule. In addition, confirmation of the postulated *syn*,s-*cis* (2a) structure of the red formazans was sought, and a contribution to the elucidation of the question of tautomerism *versus* mesomerism might be made by the solution of a suitable crystal structure.

2. Crystal and molecular structure of 3-nitro-1,5-di(2,6-dimethylphenyl)-formazan

Experimental details of the preliminary *X*-ray analysis and the collection of intensity data are given below in full for this particular structural analysis and will not be repeated for the *X*-ray structural analyses reported in Chapters III and V unless pertinent.

Crystal data

3-Nitro-1,5-di(2,6-dimethylphenyl)formazan (14) was prepared by coupling the diazonium cation of 2,6-dimethylaniline with nitromethane in 2 : 1 molar proportion, as described in the experimental section of this Chapter. The small amount of red oily product (~1% yield) was extracted into chloroform and purified by chromatography (alumina/benzene). Recrystallization from ethanol yielded dark red needles elongated along *b*, m.p. 217-220°C (Found: C, 62.55; H, 5.9; N, 21.3%. $C_{17}H_{19}N_5O_2$ requires C, 62.8; H, 5.85; N, 21.5%).

The density of the crystals was determined by the flotation method in aqueous potassium iodide. This medium was chosen to avoid possible dissolution of the crystals in organic media. The density (D_m) was read off a nomogram as 1.29 g cm^{-3}.

Several crystals were selected on the basis of their size, shape, and extinction of polarized light and mounted along their needle axes (*b*) at the tips of thin glass fibres. A two-circle optical goniometer was used for alignment. Oscillation, Weissenberg, and precession photographs were taken using a Stoe (Heidelberg) goniometer in conjunction with

Philips PW 1120 and PW 1008 *X*-ray generators operating at 20 mA and 40 kV. A copper target was used and Cu-K_α radiation (λ = 1.5418 Å) was obtained with the aid of a nickel filter. The oscillation camera radius was 2.865 cm and the *X*-ray films (Ilford Industrial G or 3M Medical) were processed in the normal way with Ilford Phenisol *X*-ray developer and Agfa Agefix fixer solutions.

After photography on several different crystals an initial estimate of the unit cell parameters was obtained. An oscillation photograph taken about the y-axis indicated a monoclinic unit cell, and careful scrutiny of an $h0l$ precession photograph revealed β to be about 91°. A single crystal of dimensions 0.4 x 0.2 x 0.2 mm was then used to obtain accurate cell parameters from a least-squares analysis of the χ, ϕ, and 2θ angles of 25 high-order reflections accurately centred on a Philips PW 1100 four-circle computer-controlled diffractometer. The same crystal was used for subsequent collection of intensity data. The final cell parameters are given in Table 3. Using these accurate values of the cell parameters in the expression

$$ZM = ND_m abc\sin\beta$$

where M is the molecular mass, N is the Avogadro constant, D_m is the measured density, and $abc\sin\beta = V$ is the volume of the unit cell, the number of molecules per unit cell (Z) was calculated to be 3.95. Hence there are four molecules in the unit cell and using this value the calculated density D_c was found to be 1.31 g cm^{-3}.

TABLE 3 : CRYSTAL DATA

Molecular formula	:	$C_{17}H_{19}N_5O_2$	
Molecular mass	:	325.4 g mol^{-1}	
Space group	:	monoclinic, $P2_1/n$	
a = 16.419(8) Å		D_m	= 1.29 g cm^{-3}
b = 7.497(4) Å		D_c	= 1.31 g cm^{-3}
c = 13.443(6) Å		μ(Mo-K_α)	= 0.53 cm^{-1}
β = 90.69(5)°		$F(000)$	= 688
V = 1654.6 Å^3			

From Weissenberg and precession photographs the conditions for non-extinction of reflections were found to be:

hkl : no conditions

$h0l$: $h + l = 2n$

$0k0$ $k = 2n$.

These conditions were subsequently confirmed by inspection of the diffractometer intensity data and thus the space group was uniquely determined as $P2_1/n$. This is a non-standard setting and is not listed in *International Tables for* X-*Ray Crystallography*.[101] The space group $P2_1/n$ is the same as $P2_1/c$ except for a different choice of the c-axis.[102] The relationship between unit cells with space groups $P2_1/n$ and $P2_1/c$ is shown in Figure 3.

Intensity data

Three-dimensional intensity data were collected on the Philips PW 1100 computer-controlled four-circle diffractometer by the ω - 2θ scan technique.

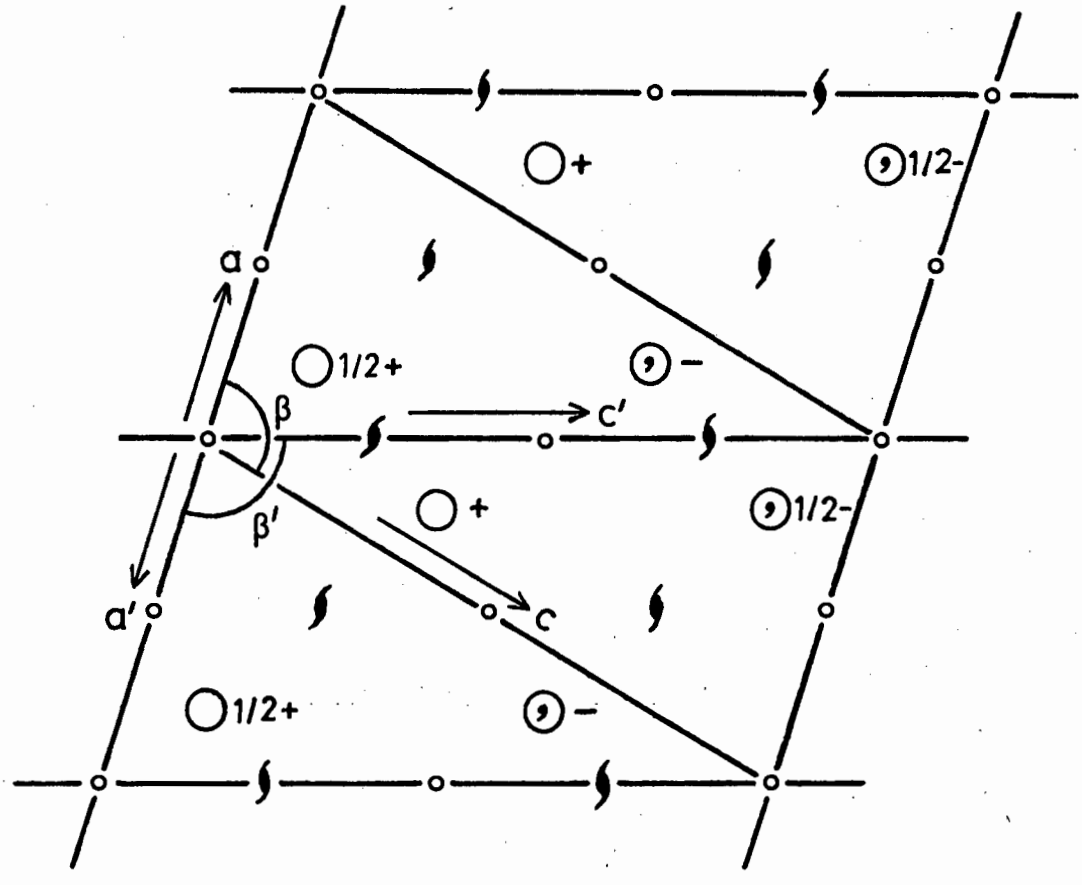


FIGURE 3 : The relationship (not drawn to scale) between the unit cell (bounded by a, b, and c) corresponding to the space group $P2_1/n$, and the unit cell (bounded by a', b', and c') corresponding to the space group $P2_1/c$. The equivalent positions are:

$P2_1/n$: x,y,z; $-x,-y,-z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

$P2_1/c$: x,y,z; $-x,-y,-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$; $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The two cells are projected onto (010). Symmetry operation symbols are taken from reference 101.

In this scanning process[103] the detector of the diffractometer rotates at an angular rate which is twice that of the crystal. In the ω-scan of a given reflection, the crystal and hence the reciprocal lattice is rotated by the ω-circle to carry the lattice point from the outside of the sphere of reflection to the inside. The ω-scan is similar to a photometric trace made parallel to the central line of the film on a zero-layer Weissenberg photograph, while the 2θ-scan corresponds to a similar trace made along the diagonal passing through reflections on a common central lattice row. In this way a reasonable number of quanta are detected during one traverse through the reflecting position.

A Philips PW 1130 4 kW *X*-ray generator operating at 50 kV and 20 mA provided the source of radiation. Molybdenum-K_α radiation (λ = 0.7107 Å) was obtained with the aid of a graphite monochromator. The take-off angle, source to crystal distance, and crystal to counter distance were 6°, 24.5 cm, and 22 cm, respectively. The receiving aperture at the counter was 2° in the 2θ plane and 1° in the plane normal to this. The diffractometer scan width was 1.2°θ and the scan speed was $0.03°\theta s^{-1}$ The intensities of three reference reflections monitored after every 68 measured reflections remained constant to within 1.3% of their mean values, indicating crystal and instrument stability during the data collection. The standard error $\sigma(I_{rel})$ in the relative integrated intensity I_{rel} was calculated from

$$\sigma(I_{rel}) = [(0.02N_o)^2 + K^2N_b + N_o]^{\frac{1}{2}}$$

where N_o is the gross peak count for a particular reflection, N_b is the background count (measured on each side of the peak), and K is the ratio of scan to background times. The background scan time on each side of

the reflection peak was equal to half the scan time over the peak. A total of 2506 reflections were collected in the range $3 \leqslant \theta \leqslant 23°$; using the criterion $I_{rel} > 2\sigma(I_{rel})$ for an observed reflection[104] and omitting systematic absences, 1143 unique reflections remained which were employed in the structural analysis.

The linear absorption coefficient μ for Mo-K_α radiation[105] was determined as 0.53 cm^{-1}. From the dimensions of the crystal used it can be seen than μR (where R is the radius of the crystal) varied between 0.01 and 0.02. The corresponding absorption correction factor A^* remained constant over the entire θ range scanned;[106] absorption corrections were therefore deemed unnecessary. Lorentz-polarization corrections were applied automatically in the process of transferring intensity data to magnetic tape. Crystal data are summarized in Table 3.

Solution and refinement of the structure

The structure was solved by the automatic centrosymmetric routine of the *SHELX 76* program system,[107] from which an E-map yielded the positions of all the heavy atoms. Complex neutral-atom scattering factors for the heavy atoms were those of Cromer and Mann;[109] for hydrogen the scattering factors of Stewart *et al.* were used. Anomalous-dispersion corrections were taken from Cromer and Liberman.[111] The final full-matrix least-squares refinement was carried out with all non-hydrogen atoms treated anisotropically. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of a reflection and F_o and F_c are observed and calculated structure factors. For the anisotropic refinement the thermal parameters were of the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$ where U_{ij} are the anisotropic temperature

factors expressed in terms of mean-square amplitudes of vibration in ångström units.

The hydrogen atoms bonded to carbon, most of which had been revealed in previous difference Fourier maps, were constrained to ride at 1.08 Å from their corresponding parent atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as two single parameters which finally refined to U = 0.100(8) Å (aromatic H) and U = 0.113(6) Å^2 (methyl H), the methyl hydrogens being refined as rigid groups. This technique of constrained least-squares refinement using bond length constraints, as well as the location and refinement of hydrogen atoms, is discussed by Sheldrick[107] and Olovsson and Jonssen.[112] Up to this point of the refinement (R = 0.070) the imino proton had been omitted from the model and a difference Fourier synthesis was then computed and plotted to locate this ultimate hydrogen atom. All atoms except the imino hydrogen atom were used in the calculation and Figure 4 gives the resulting difference electron density synthesis in two xz-planes in the region of the nitrogen atoms. There can be no doubt that the maximum electron density (1.2 e Å^{-3}) occurs mid-way between N(1) and N(5) completing a hexagonal formazan ring. It was also observed at this stage that the two N-N distances were virtually identical and midway between single and double N-N bond lengths. The imino proton, H(N1/N5), was therefore constrained to be equidistant from both N(1) and N(5) and its temperature factor was refined independently to U = 0.25(4) Å^2. The N···H distance after refinement was 1.50(3) Å.

The agreement between observed (F_o) and calculated (F_c) structure factors is expressed by the conventional residual index $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = \Sigma|\Delta|/\Sigma|F_o|$. The refinement converged to R = 0.059; R_w ($= \Sigma\omega^{\frac{1}{2}}|\Delta|/\Sigma\omega^{\frac{1}{2}}|F_o|$)

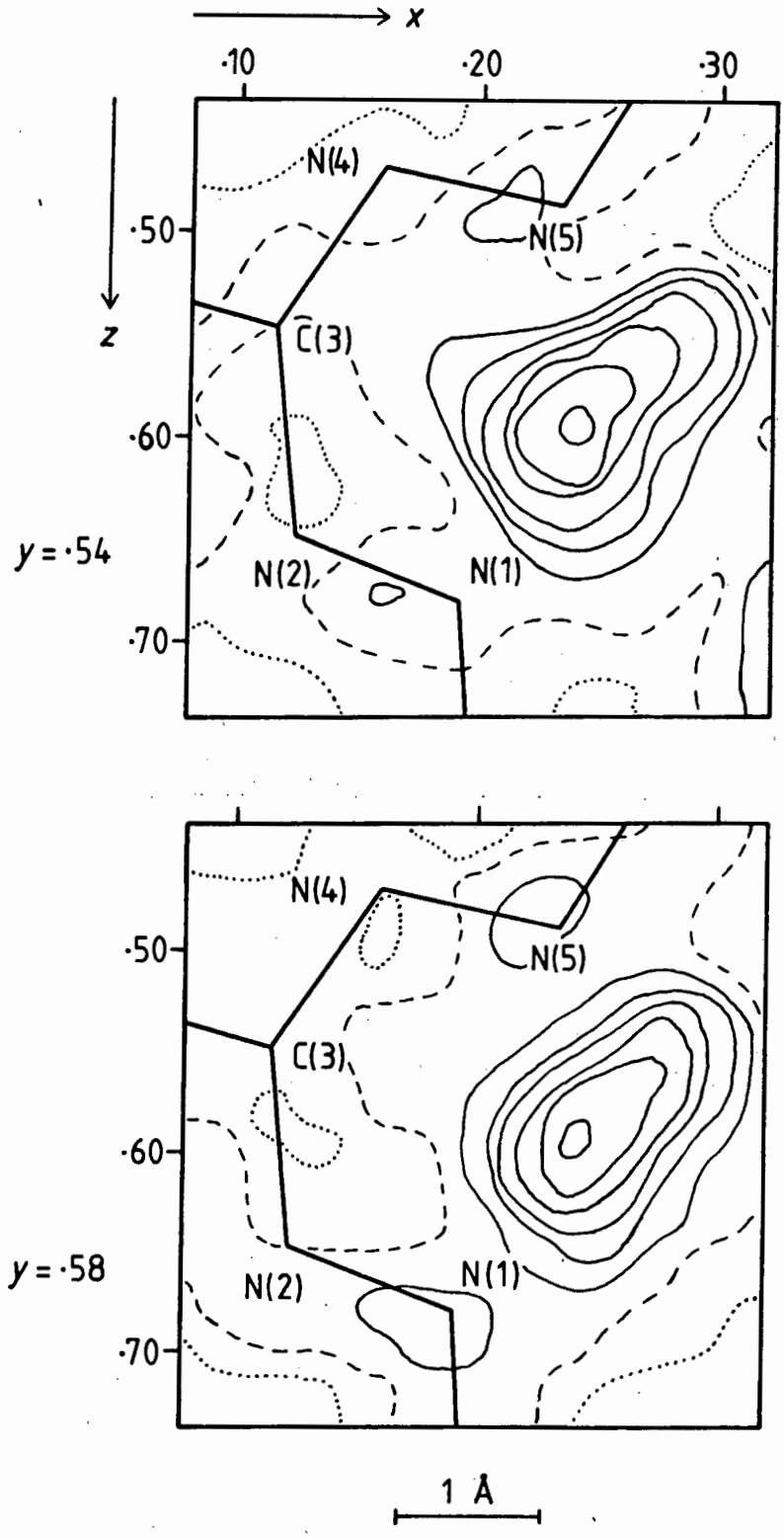
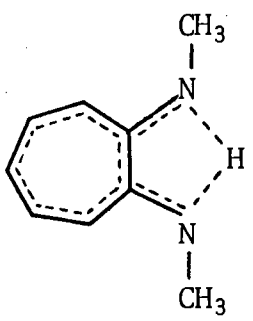


FIGURE 4 : Difference electron density map at two levels along y in the region of the nitrogen atoms after refinement with H(N1/N5) omitted from the model. Contours are at intervals of 0.02 e $Å^{-3}$; negative contours are dotted, the zero line is broken.

was 0.045 with the weighting scheme $w = 1/(\sigma^2 F_o)$ chosen to given the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o. An analysis of variance (Table 4) computed after the final cycle showed that this weighting scheme was satisfactory. In the final cycle of refinement the mean estimated standard deviation in the parameters of the non-hydrogen atoms was greater than 100 times the average parameter shift. As a final check of the correctness of the structure a difference electron density map was computed using the structure factors calculated in the last cycle of refinement. This map showed no peaks greater than 0.06 e Å^{-3}.

An alternative to this centered imino-hydrogen model (henceforth Model A) is a model in which a half-hydrogen is bonded to each terminal nitrogen atom (Model B). There are a number of reasons why this model should also be considered.

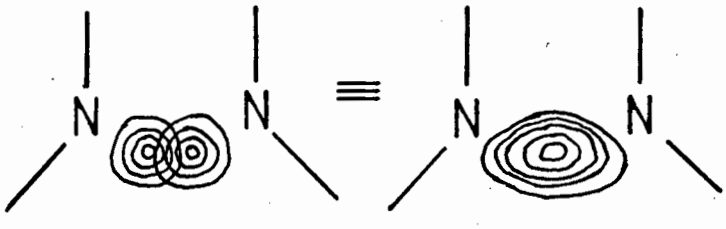
1-Methylamino-7-methylimino-1,3,5-cycloheptatriene (20) is a compound



(20)

which, like the nitroformazan(14), might undergo rapid tautomerism in solution but which appears from spectroscopic evidence to have chemically equivalent nitrogen atoms.[113] The *X*-ray structure[114] revealed the amino proton as a broad region of electron density with two maxima about 1.0 Å apart and each 1.1 Å from the nearer nitrogen atom. The structure

was refined with hydrogen atoms of weight 0.5 at these positions, but the authors point out that the saddle-point between the maxima was only about one e.s.d. lower than the maxima themselves and that two equivalent proton positions rather than a single average one was not unequivocally established. More recently, in the *X*-ray structure of the hydrochloride of the biformazan 'diformazyl' (19), the imino proton was found bound to the terminal nitrogen atoms in a site occupancy ratio of 0.65 : 0.35. Although Model A was postulated for the nitroformazan (14) on the grounds of a single fairly sharp peak found for the imino proton in the difference electron density map (Figure 4), the possibility does exist that this peak is in fact the sum of two smaller peaks resulting from half-hydrogens attached to each terminal nitrogen atom, and that the two separate peaks were not ideally resolved as they were for (19) and (20):

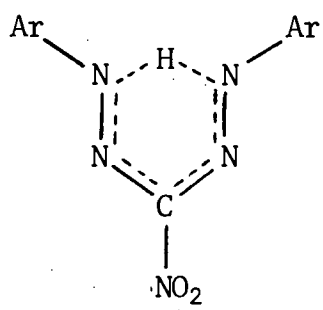


Model B would also be satisfying in providing physically reasonable N-H bond lengths, although the centered N···H···N hydrogen bond of Model A is not without precedent.[112]

The final refinement of the structure of the nitroformazan (14) was therefore repeated and the single proton constrained to be equidistant from N(1) and N(5) [H(N1/N5)] was replaced by two half-hydrogens [H(N1) and H(N5)] each fixed at 1.08 Å from the parent nitrogen atom in

sp^2 geometry. The site occupancy factors (s.o.f.'s) of H(N1) and H(N5) were tied together and refined so that their sum was always 1.0. After the same number of full-matrix least-squares refinement as used for Model A the isotropic temperature factor for the half-hydrogens H(N1) and H(N5) (refined as a single parameter) dropped to 0.11(3) Å^2 with s.o.f.'s of 0.55(7) [H(N1)] and 0.45(7) [H(N5)]. The low temperature factor compared with that for H(N1/N5) in Model A [0.25(4) Å^2] shows that Model B must be seriously considered. For this refinement U(aromatic H) = 0.102(9) Å^2 and U(methyl H) = 0.125(7) Å^2. The conventional residual index R increased slightly to 0.063 and R_w to 0.048 using the same weighting function as in Model A. The analysis of variance for the Model B refinement is given in Table 4. The two models are summarized below:

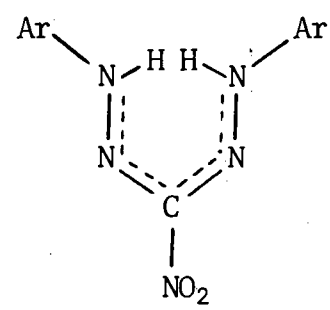
Model A



S.o.f.[H(N1/N5)] = 1.0

U[H(N1/N5)] = 0.25(4) Å^2
R = 0.059
R_w = 0.045
R_g = 0.040
No. of reflections = 1143
No. of parameters = 260
H(N1/N5) parameters refined:
x, y, z, constrained distance, U_{iso}.

Model B



S.o.f.[H(N1)] = 0.55(7)
S.o.f.[H(N5)] = 0.45(7)
U[H(N1)] = U[H(N5)] = 0.11(3) Å^2
R = 0.063
R_w = 0.048
R_g = 0.043
No. of reflections = 1143
No. of parameters = 257
H(N1) and H(N5) parameters refined:
U_{iso}, s.o.f.; thus 3 fewer parameters than Model A.

Hamilton's[115] significance test on the crystallographic *R*-factor ratio $\mathcal{R} = R_g(\text{Model B})/R_g(\text{Model A})$ may be used to determine whether the residual index *R* is *significantly* larger for the model B refinement. If there are correlations between the observed structure factors such that the variance-covariance matrix $M^{(F)}$ for the observations has elements $m_{ij} = \text{covariance}(|F_i|, |F_j|)$, then the corresponding weight matrix W is defined by $W = \sigma^2 M^{-1}$ where σ^2 is the variance of an observation of unit weight. The generalized weighted *R* factor is then defined by $R_g = (\Sigma\Sigma w_{ij}|\Delta_i||\Delta_j|/\Sigma\Sigma w_{ij}|F_{oi}||F_{oj}|)^{\frac{1}{2}}$ and this is also given as part of the *SHELX76* output. R_g is identical with R_w (defined earlier) if the weight matrix is diagonal with $w_{ii} \equiv w_i$ and $w_{ij} = 0$ for $i \neq j$.

The linear hypothesis *that the 257 parameters of Model B correctly describe the structure* may now be tested. The *R*-factor ratio $\mathcal{R} = R_g(\text{Model B})/R_g(\text{Model A}) = 0.043/0.040 = 1.075$ is formed. This value of $\mathcal{R}$ calculated is compared with the values of significance points for $\mathcal{R}$ given in tables.[116] If the value of $\mathcal{R}$ exceeds the tabulated value for significance level α, the hypothesis is rejected and the probability is less than α that the hypothesis has been rejected when actually true. The dimension of our linear hypothesis (using Hamilton's notation[115]) is $b = 257$ and the number of degrees of freedom for the refinement is $n - m = 1143 - 257 = 886$. A pertinent tabular value of $\mathcal{R}_{b,n-m,\alpha}$ obtained by interpolation[116] is $\mathcal{R}_{257,886,0.05} = 1.202$; thus the hypothesis cannot be rejected at the 5% level of significance. Examination of the tables[116] also reveals that $\mathcal{R}_{257,886,0.50} = 1.164$, indicating that the hypothesis cannot be rejected at the 50% level, *i.e.*, we would be wrong half the time if we rejected similar hypotheses at this level.

Alternatively, the linear hypothesis *that Model B is significantly different from Model A* may be tested. The dimension of the hypothesis is $m_A - m_B = 260 - 257 = 3$ and the number of degrees of freedom for the refinement is $n - m = 1143-257 = 886$. Pertinent tabular values[116] of $\mathscr{R}$ are $\mathscr{R}_{3,886,0.05} = 1.005$ and $\mathscr{R}_{3,886,0.005} = 1.008$; the hypothesis may be rejected at both the 0.05 and 0.005 levels of significance.

It must be concluded that, from a statistical point of view, there is no *significant* difference between the parameters defining Models A and B, and Hamilton[115] points out that there is then justification in taking a weighted mean of the two sets of results as the best current estimate of the true parameter set. As Hamilton observes, 'the model with the fewer restraints, that is, with the greater number of parameters *(Model A)*, can usually be made to fit the data better than can the more restrained model *(Model B)*'.[115] It has been shown here that the slightly smaller number of parameters in Model B leads to apparent deterioration in the agreement between observed and calculated structure factors which is insignificant.

It seems that there is no choice to be made between Models A and B based on the present *X*-ray diffraction data, and the results for both models are given here in full. An attempt was made to obtain low-temperature *X*-ray data, but this failed due to problems which arose with the four-circle diffractometer when operating at low temperature. In addition, all the mounted crystals fractured at low temperature even when taken down to -100°C in very gradual steps. An effort is being made to grow crystals large enough for use in a neutron diffraction experiment, the results of which should locate the position of the imino hydrogen atom unambiguously. Nevertheless, the significance of the two models

proposed here is discussed below. Tables 5 and 6 list the observed and calculated factors for Models A and B, while the final atomic positional and thermal parameters for both models are set out in Tables 7, 8, and 9.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with the programs *SHELX76*[107] (data reduction, structure determination and refinement), *XANADU*[117] (bond lengths, bond angles, torsion angles, and least-squares planes), and *PLUTO*[118] (molecular illustrations).

Molecular structure

The intramolecular bond lengths and angles for both models of the nitroformazan (14) are given in Tables 10 and 11, respectively. The molecular structure and the atomic nomenclature utilized in its description are shown in Figure 5, while Figures 6 and 7 summarize the bond lengths and angles for Models A and B, respectively.

The gross features of the structure are independent of whichever model is adopted to describe the imino proton, and the following discussion applies to both models, unless otherwise stated. If only one parameter is quoted, then it applies to both models. The formazan crystallizes in the closed *syn,*s-*cis,trans* configuration [(2c); $R^1 = R^2$ = 2,6-dimethylphenyl, $R^3 = NO_2$] with the imino proton forming an intramolecular hydrogen bridge to give a six-membered formazan ring. The nature of this hydrogen bridge will be discussed later. This configuration of the N-N-C-N-N chain is the same as that found recently[100] for the hydrochloride of 'diformazyl' (19).

TABLE 4 : ANALYSIS OF VARIANCE[a] FOR 3-NITRO-1,5-DI(2,6-DIMETHYLPHENYL)FORMAZAN (14) (Models A and B)

(a) As a function of sin θ

sin θ	0.00 - 0.16	0.16 - 0.20	0.20 - 0.22	0.22 - 0.25	0.25 - 0.27	0.27 - 0.30	0.30 - 0.32	0.32 - 0.34	0.34 - 0.36	0.36 - 0.39
N	133	131	84	127	96	145	119	107	103	98
V (Model A)	100	90	101	81	77	97	92	84	111	103
V (Model B)	119	107	105	86	80	100	92	88	112	106

(b) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.20	0.20 - 0.21	0.21 - 0.22	0.22 - 0.24	0.24 - 0.26	0.26 - 0.28	0.28 - 0.31	0.31 - 0.35	0.35 - 0.42	0.42 - 1.00
N	143	108	97	132	117	101	113	125	99	108
V (Model A)	105	101	98	95	90	84	83	80	91	105
V (Model B)	110	100	101	97	99	86	90	90	102	124

(c) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	173	119	140	147	116	166	139	143	1143
V (Model A)	91	89	93	99	98	89	99	92	94
V (Model B)	99	90	100	107	105	99	108	95	100

(d) As a function of |Miller index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	60	110	103	110	98	96	94	79	74	70	52	50	50	38	59
V (A)	96	105	100	88	93	80	83	91	98	98	78	99	98	74	111
V (B)	97	113	112	99	109	90	90	96	101	97	78	103	105	74	115

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	134	225	217	197	151	118	65	29	7	0	0	0	0	0	0
V (A)	96	100	91	94	86	90	96	108	100	0	0	0	0	0	0
V (B)	103	108	103	102	89	93	94	106	99	0	0	0	0	0	0

$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	71	139	134	120	115	104	103	86	80	64	52	35	19	16	5
V (A)	98	91	88	96	87	100	93	95	102	85	96	89	116	112	50
V (B)	100	102	97	102	97	110	100	99	104	87	96	90	122	116	60

[a] *N* = No. of reflections in the group

V = $100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections.

TABLE 5 : OBSERVED AND CALCULATED STRUCTURE FACTORS FOR MODEL A

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	0	76	75	6	0	0	37	38	15	4	0	7	-5	-7	1	1	11	-12	-1	2	1	110	109
0	4	0	76	-73	6	1	0	15	15	16	1	0	7	-3	-7	3	1	15	-14	-1	3	1	30	-29
0	6	0	19	-22	6	2	0	39	-40	17	1	0	7	-7	-7	5	1	9	8	-1	4	1	33	34
0	8	0	8	6	6	3	0	7	7	-17	0	1	8	-11	-7	6	1	7	-5	-1	7	1	9	10
1	8	0	7	6	6	4	0	20	-19	-16	2	1	7	5	-7	7	1	8	-8	0	8	1	10	-12
1	6	0	12	12	6	5	0	12	12	-15	0	1	8	9	-6	6	1	7	-7	0	6	1	16	-17
1	4	0	23	-22	6	7	0	7	-8	-15	1	1	9	-8	-6	5	1	8	-9	0	5	1	28	29
1	3	0	33	32	7	7	0	6	-6	-14	5	1	13	14	-6	4	1	15	-15	0	4	1	36	36
1	2	0	144	-145	7	4	0	11	-10	-14	3	1	19	20	-6	3	1	6	-7	0	3	1	5	5
2	1	0	69	72	7	3	0	15	15	-14	1	1	19	-19	-6	2	1	11	-11	0	2	1	166	163
2	2	0	90	-90	7	1	0	14	-14	-13	1	1	17	18	-6	1	1	8	-8	0	1	1	52	54
2	3	0	25	25	8	0	0	75	74	-13	3	1	7	8	-5	0	1	62	-62	1	1	1	42	-42
2	4	0	46	46	8	1	0	10	10	-12	5	1	16	-17	-5	3	1	25	-25	1	2	1	56	56
2	5	0	6	-9	8	2	0	6	-6	-12	2	1	20	-20	-5	4	1	11	11	1	3	1	11	13
2	6	0	18	19	8	3	0	6	-7	-12	1	1	18	18	-5	6	1	14	14	1	4	1	24	-24
2	8	0	7	-4	9	7	0	7	6	-11	0	1	21	-21	-4	7	1	8	-9	1	6	1	11	-12
3	5	0	16	-16	9	6	0	6	-7	-11	1	1	12	11	-4	6	1	9	-8	1	7	1	13	-14
3	4	0	25	25	9	5	0	11	-11	-11	3	1	10	-9	-4	5	1	8	7	2	8	1	8	10
3	3	0	42	-43	9	2	0	10	-9	-11	4	1	7	6	-4	4	1	19	20	2	6	1	11	11
3	2	0	10	-9	9	1	0	20	20	-11	5	1	7	8	-4	3	1	44	42	2	5	1	6	-7
3	1	0	19	20	10	0	0	10	10	-10	5	1	8	8	-4	2	1	13	-13	2	4	1	35	-35
4	0	0	7	-7	10	1	0	21	21	-10	4	1	12	12	-4	1	1	17	-18	2	3	1	20	-20
4	2	0	10	-10	10	2	0	12	-11	-10	2	1	5	-4	-3	0	1	50	-51	2	2	1	79	-77
4	3	0	26	-26	10	4	0	6	-6	-9	0	1	13	-14	-3	1	1	58	59	2	1	1	76	-79
4	4	0	17	18	11	2	0	14	-15	-9	1	1	14	13	-3	2	1	25	24	3	0	1	26	-26
4	5	0	14	15	11	1	0	11	11	-9	2	1	17	17	-3	4	1	26	-27	3	1	1	46	-47
4	6	0	6	-7	12	0	0	15	-15	-9	5	1	8	8	-3	5	1	10	-9	3	2	1	5	6
4	7	0	7	8	12	1	0	13	12	-9	6	1	11	-8	-2	8	1	7	5	3	3	1	5	5
5	7	0	6	5	13	5	0	8	6	-9	7	1	7	-3	-2	6	1	15	15	3	4	1	19	-19
5	5	0	11	11	13	4	0	10	10	-8	7	1	8	-7	-2	4	1	20	19	3	5	1	11	11
5	4	0	7	-5	13	2	0	8	9	-8	6	1	8	8	-2	3	1	25	-25	3	7	1	7	5
5	3	0	18	-18	14	0	0	11	11	-8	4	1	10	9	-2	2	1	76	-76	4	6	1	8	9
5	2	0	20	19	14	1	0	8	-10	-8	3	1	6	4	-2	1	1	44	43	4	5	1	5	-5
5	1	0	27	-27	14	3	0	7	-6	-7	0	1	61	-62	-1	1	1	15	-15	4	4	1	7	9

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	3	1	26	25	13	0	1	17	-17	-8	0	2	6	-3	-1	5	2	18	-17	4	5	2	9	9
4	2	1	58	-58	13	4	1	12	13	-8	1	2	18	-17	-1	4	2	27	26	4	6	2	6	-5
4	1	1	38	-38	14	2	1	6	3	-8	2	2	12	-12	-1	3	2	35	34	4	7	2	7	-6
5	0	1	95	-95	14	1	1	11	10	-8	3	2	8	-6	-1	2	2	92	90	5	5	2	9	-8
5	2	1	6	7	15	0	1	7	-5	-8	7	2	13	13	-1	1	2	91	92	5	4	2	30	-30
5	3	1	5	-4	15	3	1	7	-4	-7	6	2	8	-8	0	0	2	35	35	5	2	2	8	9
5	4	1	10	10	-16	0	2	8	-7	-7	5	2	7	8	0	1	2	5	3	6	1	2	7	-6
5	5	1	17	-17	-16	1	2	10	10	-7	4	2	15	-15	0	2	2	42	-43	6	2	2	31	-31
6	6	1	8	-9	-16	3	2	6	6	-7	3	2	8	-8	0	3	2	33	-33	6	3	2	16	-16
6	4	1	22	21	-15	3	2	7	-5	-7	1	2	11	-10	0	4	2	17	16	6	4	2	18	18
6	3	1	15	-14	-15	1	2	15	16	-6	0	2	9	9	0	5	2	12	-12	6	5	2	6	6
6	2	1	13	13	-14	1	2	20	-20	-6	3	2	12	13	0	7	2	7	9	6	6	2	14	14
6	1	1	33	-32	-14	2	2	14	14	-6	5	2	22	-22	1	5	2	14	14	7	4	2	17	18
7	1	1	14	-14	-14	3	2	19	-20	-6	7	2	6	-7	1	4	2	21	-20	7	3	2	29	28
7	2	1	52	51	-13	5	2	13	12	-5	6	2	8	10	1	3	2	19	-19	7	2	2	51	51
7	6	1	21	-20	-13	4	2	11	-11	-5	5	2	10	9	1	2	2	60	-61	8	0	2	77	74
8	5	1	7	7	-13	2	2	14	14	-5	4	2	26	-25	1	1	2	98	-100	8	1	2	41	41
8	4	1	11	-11	-13	1	2	19	-19	-5	3	2	5	5	2	0	2	18	18	8	2	2	6	6
8	1	1	29	28	-12	0	2	17	17	-5	1	2	18	16	2	1	2	26	26	8	4	2	12	-12
9	0	1	24	-23	-12	1	2	10	10	-4	0	2	29	30	2	2	2	54	-54	8	5	2	12	-13
9	1	1	13	-13	-12	3	2	36	37	-4	1	2	18	-19	2	4	2	21	-21	9	5	2	11	10
9	2	1	10	9	-12	4	2	18	-19	-4	2	2	17	-17	2	5	2	9	-9	9	4	2	11	-9
9	3	1	17	18	-12	5	2	6	6	-4	3	2	34	34	2	6	2	17	-17	9	2	2	21	-21
9	4	1	8	8	-11	5	2	13	-13	-4	4	2	12	13	2	8	2	7	4	9	1	2	24	-24
9	6	1	6	4	-11	4	2	9	-10	-4	5	2	9	8	3	6	2	7	8	10	0	2	8	-8
9	7	1	7	-8	-11	2	2	7	7	-3	7	2	6	1	3	5	2	7	-7	10	1	2	14	14
10	4	1	6	-9	-10	0	2	13	13	-3	5	2	14	-13	3	4	2	6	4	11	5	2	11	-9
10	1	1	10	-10	-10	2	2	6	-8	-3	4	2	24	-24	3	3	2	28	-28	11	3	2	16	-17
11	0	1	9	11	-10	3	2	9	8	-3	2	2	59	59	3	2	2	53	55	11	2	2	14	15
11	1	1	11	-11	-10	5	2	8	-9	-3	1	2	29	28	3	1	2	31	31	11	1	2	14	15
12	6	1	8	9	-10	6	2	10	9	-2	0	2	71	71	4	0	2	62	62	12	0	2	8	8
12	3	1	10	9	-9	5	2	9	-9	-2	2	2	55	-54	4	1	2	19	-19	12	1	2	14	-13
12	2	1	19	-18	-9	2	2	8	9	-2	3	2	22	21	4	3	2	5	-3	12	3	2	11	-9
12	1	1	8	-8	-9	1	2	11	11	-2	6	2	12	12	4	4	2	5	4	13	4	2	8	-9

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
13	3	2	7	6	-6	2	3	37	-37	2	5	3	13	-15	8	5	3	11	9	-10	0	4	7	8
14	3	2	9	10	-6	1	3	35	-35	2	4	3	25	25	8	3	3	6	5	-10	2	4	12	12
15	3	2	6	2	-5	0	3	7	-7	2	3	3	15	-15	8	2	3	18	17	-10	5	4	9	-11
16	0	2	7	-6	-5	1	3	40	41	2	2	3	4	-3	8	1	3	11	-12	-9	5	4	6	4
-17	1	3	9	-9	-5	2	3	21	21	3	0	3	44	-43	9	0	3	9	7	-9	1	4	5	-5
-16	3	3	7	9	-5	3	3	13	12	3	1	3	9	-9	9	1	3	27	-25	-8	2	4	11	12
-15	0	3	17	16	-5	5	3	16	16	3	2	3	15	15	9	2	3	6	-6	-8	3	4	15	16
-14	2	3	13	-13	-4	4	3	23	23	3	3	3	7	6	9	3	3	16	-17	-8	4	4	8	7
-13	1	3	8	10	-4	3	3	19	-18	3	5	3	11	10	9	4	3	11	-11	-8	5	4	7	-9
-13	2	3	10	-9	-4	2	3	19	-20	3	6	3	8	7	10	6	3	7	7	-8	6	4	6	-7
-12	4	3	16	17	-4	1	3	12	12	3	7	3	10	10	10	4	3	14	14	-8	7	4	7	-4
-12	3	3	12	-13	-3	0	3	87	-88	4	5	3	20	20	10	2	3	5	-3	-7	6	4	7	-5
-12	2	3	7	3	-3	1	3	35	35	4	4	3	21	20	10	1	3	11	-12	-7	5	4	7	-6
-12	1	3	21	-20	-3	2	3	13	13	4	3	3	21	20	11	0	3	14	14	-7	4	4	15	-13
-11	0	3	7	-8	-3	5	3	5	3	4	2	3	27	-27	11	1	3	10	12	-7	2	4	24	24
-11	1	3	7	8	-2	5	3	12	12	4	1	3	7	8	11	3	3	12	14	-7	1	4	35	35
-11	5	3	9	7	-2	4	3	12	12	5	0	3	23	-23	12	1	3	11	10	-6	0	4	19	19
-10	2	3	6	-6	-2	1	3	35	35	5	1	3	10	10	13	2	3	6	5	-6	1	4	53	-52
-10	1	3	7	4	-1	0	3	45	-46	5	2	3	19	18	13	3	3	6	-5	-6	3	4	17	-17
-9	0	3	13	13	-1	2	3	20	20	5	3	3	13	13	13	4	3	8	6	-6	7	4	8	9
-9	1	3	6	6	-1	3	3	19	19	5	4	3	6	-6	15	0	3	7	-6	-5	7	4	7	4
-9	5	3	11	12	-1	5	3	11	11	5	5	3	13	-13	16	2	3	6	-3	-5	6	4	6	9
-8	5	3	15	-15	-1	6	3	7	9	5	6	3	7	-4	-16	0	4	14	-14	-5	5	4	13	12
-8	2	3	26	-28	0	5	3	11	-11	6	6	3	11	12	-16	2	4	8	7	-5	3	4	10	11
-8	1	3	15	15	0	4	3	11	-11	6	4	3	9	10	-15	1	4	8	9	-5	2	4	35	34
-7	0	3	19	19	0	3	3	21	-21	6	3	3	11	-11	-14	0	4	15	-15	-5	1	4	63	-62
-7	1	3	12	-11	0	2	3	70	-69	6	2	3	32	-32	-14	1	4	8	-8	-4	1	4	29	29
-7	2	3	7	7	0	1	3	5	4	6	1	3	39	38	-13	2	4	26	26	-4	2	4	21	-20
-7	3	3	42	-43	1	0	3	22	-23	7	0	3	37	-37	-13	1	4	19	-19	-4	3	4	45	44
-7	6	3	6	5	1	1	3	63	-63	7	1	3	24	-24	-12	0	4	6	-6	-4	6	4	8	-7
-6	6	3	7	-5	1	2	3	21	-20	7	2	3	13	14	-12	3	4	6	6	-3	5	4	6	-4
-6	5	3	18	19	1	3	3	49	-50	7	4	3	20	20	-12	4	4	8	-8	-3	4	4	24	-25
-6	4	3	10	11	1	4	3	38	-40	7	7	3	6	3	-11	3	4	9	10	-3	3	4	12	12
-6	3	3	26	26	1	5	3	9	-9	8	6	3	9	-12	-11	1	4	6	4	-3	2	4	18	-18

TABLE 5 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	1	4	22	-23	3	1	4	21	21	15	2	4	6	-4	-4	3	5	8	-7	3	2	5	20	19
-2	0	4	22	-21	4	1	4	8	-7	-15	0	5	7	6	-4	2	5	7	-6	3	3	5	17	-16
-2	1	4	23	23	4	2	4	9	8	-15	1	5	7	4	-4	1	5	16	-16	3	4	5	5	-6
-2	2	4	13	-12	4	3	4	23	-22	-14	3	5	7	-3	-3	0	5	43	44	3	5	5	10	12
-2	3	4	15	15	4	4	4	23	22	-14	1	5	8	-8	-3	1	5	19	-19	3	7	5	11	11
-2	4	4	30	29	5	4	4	14	-15	-13	0	5	18	-18	-3	2	5	16	16	4	3	5	14	14
-1	6	4	8	-9	5	3	4	17	17	-13	1	5	7	9	-3	3	5	23	-23	4	2	5	31	-31
-1	4	4	7	-7	5	2	4	22	23	-13	2	5	17	-16	-3	4	5	15	-16	4	1	5	8	7
-1	3	4	13	-13	5	1	4	9	-10	-12	3	5	7	-5	-2	5	5	8	5	5	1	5	5	5
-1	2	4	47	47	6	0	4	3	-5	-12	2	5	7	-2	-2	4	5	8	8	5	2	5	11	-11
-1	1	4	5	5	6	1	4	12	17	-12	1	5	12	13	-2	2	5	11	-13	5	3	5	9	8
0	0	4	75	75	6	2	4	5	-5	-11	0	5	30	31	-2	1	5	13	-12	6	4	5	12	12
0	1	4	12	-11	6	3	4	6	8	-11	2	5	9	11	-1	0	5	25	25	6	3	5	5	-6
0	2	4	10	-10	7	3	4	8	10	-11	3	5	9	-9	-1	1	5	23	23	6	2	5	13	-13
0	3	4	24	-25	7	2	4	20	21	-10	1	5	11	12	-1	2	5	5	-2	7	1	5	9	9
0	4	4	27	-28	8	0	4	11	-10	-9	0	5	16	15	-1	3	5	5	5	7	2	5	8	-8
0	5	4	8	-9	8	3	4	18	-18	-9	2	5	10	-10	-1	4	5	18	-18	7	4	5	7	8
0	6	4	18	-19	8	5	4	12	-12	-9	3	5	14	-15	-1	5	5	12	-12	7	5	5	9	-6
1	7	4	7	-7	9	5	4	10	-10	-9	4	5	9	-11	0	6	5	8	-8	8	6	5	8	-8
1	6	4	7	-4	9	4	4	8	-5	-9	5	5	6	5	0	5	5	7	-8	8	5	5	8	-9
1	5	4	13	-13	9	3	4	12	-13	-8	4	5	9	7	0	3	5	18	-18	8	3	5	12	-12
1	4	4	24	-25	10	0	4	23	-23	-8	3	5	11	10	0	2	5	19	-19	8	2	5	8	-7
1	3	4	12	-12	10	1	4	10	9	-8	2	5	16	-15	0	1	5	10	11	8	1	5	14	14
1	2	4	9	9	10	2	4	8	-8	-7	1	5	18	17	1	0	5	6	-6	9	1	5	7	5
1	1	4	4	-1	10	3	4	15	14	-7	3	5	8	-7	1	1	5	21	21	9	2	5	18	-18
2	0	4	41	-41	10	5	4	7	6	-7	4	5	5	5	1	3	5	32	31	9	3	5	8	10
2	1	4	30	30	11	5	4	6	2	-6	4	5	17	16	1	5	5	7	3	9	4	5	15	-14
2	2	4	24	-24	11	2	4	18	19	-6	3	5	19	-19	2	7	5	11	9	10	4	5	11	10
2	3	4	36	37	12	0	4	11	10	-5	0	5	23	-23	2	4	5	11	11	11	0	5	16	17
2	4	4	16	16	12	1	4	7	-10	-5	1	5	8	7	2	3	5	9	-8	11	3	5	7	-8
2	5	4	10	11	12	2	4	7	8	-5	2	5	11	-11	2	2	5	17	-18	12	2	5	13	-12
2	6	4	7	7	12	3	4	11	-11	-5	3	5	6	-5	2	1	5	17	17	12	1	5	13	15
3	6	4	13	15	13	2	4	6	5	-5	4	5	9	-9	3	0	5	65	64	13	2	5	7	-7
3	3	4	23	23	13	1	4	8	-7	-4	7	5	7	-5	3	1	5	40	-39	13	3	5	9	-8

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
14	3	5	6	-1	-3	5	6	7	-7	2	6	6	6	6	14	0	6	9	-6	-3	5	7	12	-13
15	0	5	7	6	-3	4	6	6	-7	3	5	6	14	-14	14	1	6	10	-12	-3	6	7	12	11
15	1	5	8	8	-3	2	6	5	5	3	3	6	6	-6	15	3	6	8	9	-2	5	7	10	11
-16	0	6	7	-7	-3	1	6	39	38	3	2	6	7	8	15	1	6	11	-8	-2	4	7	7	-6
-14	0	6	22	-22	-2	0	6	42	-43	3	1	6	55	54	-15	0	7	10	10	-2	2	7	6	-5
-14	1	6	6	-6	-2	1	6	9	-10	4	0	6	19	-19	-14	1	7	9	-8	-1	0	7	10	-10
-12	0	6	9	9	-2	2	6	8	-7	4	1	6	14	-14	-13	0	7	14	14	-1	2	7	7	-4
-12	2	6	13	12	-2	3	6	6	-3	4	2	6	22	22	-13	1	7	13	13	-1	5	7	9	-6
-12	3	6	10	10	-2	4	6	21	21	4	3	6	13	-14	-13	3	7	8	5	0	5	7	8	-6
-11	3	6	11	12	-2	5	6	7	-6	4	6	6	10	-12	-12	1	7	14	14	0	4	7	12	13
-11	2	6	7	10	-2	6	6	7	8	5	6	6	7	2	-11	1	7	10	8	0	3	7	17	-16
-11	1	6	13	14	-2	7	6	10	-9	5	4	6	14	-14	-11	4	7	11	11	0	2	7	28	28
-10	0	6	11	-11	-1	6	6	11	-11	5	1	6	26	-25	-10	3	7	6	-7	0	1	7	14	13
-10	5	6	10	-8	-1	3	6	5	4	6	0	6	37	-38	-9	0	7	13	12	1	0	7	58	57
-9	3	6	7	-7	-1	2	6	45	44	6	1	6	7	-8	-9	1	7	8	5	1	1	7	27	-26
-9	2	6	7	-6	-1	1	6	9	-8	6	5	6	8	7	-9	4	7	15	-15	1	3	7	13	-14
-8	0	6	17	-17	0	0	6	37	36	7	4	6	10	-10	-8	6	7	8	5	1	4	7	17	-17
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-8	3	6	6	5	0	2	6	10	10	7	2	6	11	11	-7	2	7	7	-6	2	3	7	8	8
-7	4	6	6	-3	0	3	6	17	-18	7	1	6	14	-14	-7	4	7	8	-7	2	2	7	11	-9
-6	0	6	41	-40	0	4	6	13	-12	8	1	6	8	8	-6	5	7	9	-7	3	0	7	24	24
-6	1	6	16	-17	0	5	6	7	6	8	3	6	6	8	-6	4	7	6	-5	3	1	7	12	11
-6	2	6	16	-16	0	6	6	12	-12	8	4	6	9	-11	-6	2	7	10	-11	3	2	7	12	-13
-6	4	6	6	4	1	6	6	12	13	9	3	6	7	-3	-6	1	7	8	-7	3	3	7	20	20
-5	5	6	10	7	1	5	6	22	23	9	1	6	17	-18	-5	0	7	6	-4	3	4	7	6	8
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-5	2	6	13	12	1	2	6	28	-28	11	2	6	9	-8	-4	3	7	10	10	4	1	7	11	-10
-5	1	6	36	-36	1	1	6	57	-57	11	1	6	27	29	-4	2	7	14	14	5	0	7	9	10
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-4	2	6	14	15	2	1	6	25	24	12	1	6	10	-9	-3	0	7	16	15	5	2	7	20	-20
-4	3	6	9	8	2	2	6	15	15	12	2	6	11	10	-3	1	7	21	20	5	4	7	8	-9
-4	5	6	6	-3	2	3	6	16	16	13	3	6	6	-4	-3	2	7	6	5	5	5	7	11	-11
-4	6	6	16	-16	2	4	6	14	13	13	2	6	8	7	-3	3	7	7	8	6	5	7	6	3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	3	7	8	-9	-6	0	8	6	-6	4	0	8	36	-35	-11	4	9	7	-8	0	3	9	8	8
6	2	7	7	-6	-6	1	8	12	-14	4	1	8	17	-17	-10	4	9	8	-7	0	2	9	8	8
7	0	7	14	14	-5	6	8	7	8	4	2	8	5	4	-10	3	9	7	-8	1	0	9	13	13
7	3	7	6	-5	-5	4	8	6	-3	4	3	8	14	-12	-9	5	9	9	7	1	2	9	10	-10
7	6	7	7	-8	-4	2	8	7	8	5	4	8	12	-12	-8	5	9	7	-4	1	3	9	6	4
8	5	7	7	6	-4	3	8	14	12	5	1	8	8	-8	-8	2	9	8	4	1	4	9	7	7
8	3	7	7	-8	-4	4	8	15	16	6	0	8	26	-26	-7	0	9	7	7	1	5	9	9	-9
8	2	7	6	6	-4	5	8	6	6	6	2	8	7	3	-7	3	9	9	-9	2	2	9	6	3
8	1	7	13	-14	-3	6	8	6	-8	6	4	8	11	11	-6	4	9	6	8	3	0	9	10	9
9	2	7	13	-13	-3	5	8	8	9	6	6	8	10	12	-6	3	9	7	7	3	2	9	9	-10
9	3	7	9	8	-3	4	8	13	-13	7	5	8	7	-8	-6	2	9	7	7	3	3	9	7	-8
10	3	7	10	10	-3	3	8	19	19	7	4	8	18	19	-6	1	9	12	-12	5	0	9	10	10
10	1	7	16	16	-3	2	8	11	-12	7	3	8	7	5	-5	0	9	19	19	5	5	9	7	-8
11	0	7	47	47	-3	1	8	7	-7	7	2	8	20	20	-5	1	9	20	20	6	4	9	9	-8
11	1	7	6	6	-2	0	8	14	-15	7	1	8	9	9	-5	2	9	15	16	6	2	9	8	-7
12	2	7	9	-11	-2	2	8	10	-8	8	0	8	9	10	-5	3	9	16	15	7	0	9	17	-19
12	1	7	9	-8	-2	3	8	8	-10	8	2	8	12	13	-4	5	9	7	9	7	2	9	14	-16
13	0	7	8	-9	-1	6	8	7	6	8	3	8	15	-14	-4	4	9	13	-14	7	3	9	10	10
13	1	7	13	12	-1	5	8	17	-16	8	4	8	18	-20	-4	2	9	18	-17	7	4	9	19	19
13	2	7	12	-12	-1	4	8	16	17	9	5	8	16	15	-4	1	9	10	9	8	5	9	8	-7
14	3	7	9	-7	-1	3	8	7	-9	9	2	8	26	-26	-3	0	9	23	-24	8	2	9	35	35
14	1	7	10	6	-1	1	8	13	15	9	1	8	9	-9	-3	1	9	14	-14	9	0	9	46	47
-14	1	8	7	-8	0	0	8	23	-22	10	0	8	13	-13	-3	3	9	9	-10	9	3	9	8	-7
-13	2	8	10	12	0	3	8	10	-10	10	1	8	8	9	-3	4	9	11	13	9	4	9	9	-10
-12	0	8	8	13	1	4	8	8	11	10	2	8	21	22	-2	5	9	8	-7	10	3	9	10	12
-12	3	8	9	9	1	3	8	7	-8	10	3	8	19	19	-2	4	9	6	-5	10	1	9	7	-8
-11	4	8	7	-7	1	2	8	9	8	10	4	8	9	8	-2	3	9	10	-9	11	1	9	13	11
-11	2	8	17	-18	2	2	8	20	19	11	3	8	10	-10	-2	2	9	22	22	11	2	9	9	-10
-10	0	8	8	-7	2	4	8	8	-9	11	2	8	10	12	-1	0	9	10	10	12	2	9	12	-12
-10	5	8	7	-5	2	6	8	10	-9	11	1	8	14	15	-1	2	9	16	-16	13	1	9	7	5
-9	4	8	8	10	3	6	8	9	10	12	0	8	18	-18	-1	3	9	27	28	-12	0	10	7	6
-9	1	8	6	-4	3	5	8	7	4	12	1	8	20	-19	-1	4	9	17	-18	-9	3	10	8	-5
-8	1	8	6	1	3	2	8	16	-16	12	3	8	10	-9	-1	5	9	8	7	-9	2	10	8	-9
-7	2	8	6	-6	3	1	8	7	-6	13	1	8	12	-12	0	4	9	7	-6	-8	2	10	8	6

TABLE 5 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-8	4	10	7	6	0	2	10	13	13	-7	1	11	11	10	5	2	11	7	-5	5	2	12	7	-10
-7	3	10	9	-8	0	3	10	15	-14	-6	3	11	8	-8	6	2	11	11	13	6	0	12	19	-19
-7	1	10	20	20	1	5	10	7	8	-6	1	11	11	11	6	1	11	12	-12	6	3	12	7	3
-6	1	10	24	-23	2	4	10	8	-9	-5	0	11	20	-20	7	0	11	7	9	-7	0	13	12	-10
-6	2	10	7	-5	3	5	10	7	-8	-5	1	11	15	-16	7	2	11	7	-9	-5	0	13	13	-12
-6	3	10	19	-20	3	2	10	12	-11	-5	2	11	6	7	8	2	11	7	-6	-5	1	13	8	-5
-6	4	10	12	11	3	1	10	7	6	-5	3	11	12	-13	8	1	11	7	5	-3	0	13	10	-7
-5	5	10	14	14	5	3	10	7	8	-5	4	11	8	7	10	1	11	7	-3	-3	1	13	9	-9
-5	4	10	10	9	5	2	10	8	-7	-4	2	11	16	16	-9	1	12	9	10	-1	0	13	17	16
-5	3	10	16	17	6	1	10	10	13	-4	1	11	11	-10	-8	0	12	7	7	-1	2	13	10	9
-5	2	10	20	20	6	2	10	7	6	-3	3	11	14	15	-6	2	12	13	-13	0	3	13	6	6
-5	1	10	23	-23	6	4	10	7	-10	-3	4	11	10	-10	-4	1	12	8	5	1	0	13	14	-14
-4	0	10	47	48	6	5	10	8	8	-2	2	11	15	14	-4	2	12	7	-3	1	3	13	8	7
-4	1	10	9	10	7	5	10	7	-2	-2	1	11	25	-26	-4	3	12	9	-10	2	3	13	10	-9
-4	2	10	8	7	7	4	10	8	5	-1	0	11	8	7	-3	1	12	17	-16	3	1	13	14	-14
-4	4	10	12	-12	7	2	10	13	-13	0	3	11	10	11	-2	0	12	16	-16	4	3	13	7	2
-3	5	10	11	-11	7	1	10	9	8	0	2	11	13	-12	-1	3	12	6	-1	4	1	13	8	-5
-3	2	10	37	-37	8	0	10	29	-29	0	1	11	15	16	-1	1	12	18	17	6	1	13	8	-7
-2	0	10	30	-30	8	4	10	8	7	1	5	11	7	-7	0	0	12	23	24	7	0	13	8	6
-2	1	10	24	24	9	4	10	10	7	2	3	11	6	-4	0	2	12	12	12	-2	1	14	9	9
-2	2	10	13	-16	9	2	10	12	14	2	2	11	9	6	2	3	12	11	-10	-1	1	14	9	8
-2	3	10	11	12	10	2	10	7	7	3	2	11	6	5	3	4	12	10	9	1	2	14	7	-7
-1	4	10	12	14	11	2	10	9	-8	3	3	11	7	6	3	3	12	9	6	1	1	14	7	-7
-1	3	10	15	-17	-11	0	11	10	-9	4	4	11	9	-10	5	3	12	9	-9	2	1	14	7	6
-1	2	10	7	8	-8	3	11	11	11	5	1	11	10	-11										

TABLE 6 : OBSERVED AND CALCULATED STRUCTURE FACTORS FOR MODEL B

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	0	76	77	6	0	0	37	37	15	4	0	7	-5	-7	1	1	11	-12	-1	2	1	110	108
0	4	0	76	-73	6	1	0	15	15	16	1	0	7	-3	-7	3	1	15	-14	-1	3	1	30	-29
0	6	0	19	-22	6	2	0	39	-41	17	1	0	7	-7	-7	5	1	9	8	-1	4	1	33	33
0	8	0	8	6	6	3	0	7	7	-17	0	1	8	-10	-7	6	1	7	-5	-1	7	1	9	10
1	8	0	7	6	6	4	0	20	-19	-16	2	1	7	5	-7	7	1	8	-8	0	8	1	10	-12
1	6	0	12	12	6	5	0	12	11	-15	0	1	8	9	-6	6	1	7	-7	0	6	1	16	-17
1	4	0	23	-23	6	7	0	7	-8	-15	1	1	9	-8	-6	5	1	8	-8	0	5	1	28	29
1	3	0	33	33	7	7	0	6	-5	-14	5	1	13	14	-6	4	1	15	-15	0	4	1	36	36
1	2	0	144	-145	7	4	0	11	-10	-14	3	1	19	20	-6	3	1	6	-7	0	3	1	5	5
2	1	0	69	72	7	3	0	15	14	-14	1	1	19	-18	-6	2	1	11	-11	0	2	1	166	163
2	2	0	90	-89	7	1	0	14	-15	-13	1	1	17	18	-6	1	1	8	-8	0	1	1	52	53
2	3	0	25	25	8	0	0	75	74	-13	3	1	7	7	-5	0	1	62	-63	1	1	1	42	-43
2	4	0	46	46	8	1	0	10	9	-12	5	1	16	-17	-5	3	1	25	-25	1	2	1	56	56
2	5	0	6	-8	8	2	0	6	-6	-12	2	1	20	-21	-5	4	1	11	11	1	3	1	11	13
2	6	0	18	19	8	3	0	6	-7	-12	1	1	18	18	-5	6	1	14	14	1	4	1	24	-24
2	8	0	7	-4	9	7	0	7	6	-11	0	1	21	-21	-4	7	1	8	-9	1	6	1	11	-12
3	5	0	16	-16	9	6	0	6	-7	-11	1	1	12	11	-4	6	1	9	-8	1	7	1	13	-14
3	4	0	25	25	9	5	0	11	-11	-11	3	1	10	-9	-4	5	1	8	7	2	8	1	8	10
3	3	0	42	-43	9	2	0	10	-9	-11	4	1	7	6	-4	4	1	19	20	2	6	1	11	11
3	2	0	10	-9	9	1	0	20	20	-11	5	1	7	8	-4	3	1	44	42	2	5	1	6	-6
3	1	0	19	20	10	0	0	10	10	-10	5	1	8	8	-4	2	1	13	-13	2	4	1	35	-34
4	0	0	7	-7	10	1	0	21	21	-10	4	1	12	12	-4	1	1	17	-18	2	3	1	20	-20
4	2	0	10	-10	10	2	0	12	-11	-10	2	1	5	-5	-3	0	1	50	-51	2	2	1	78	-77
4	3	0	26	-26	10	4	0	6	-6	-9	0	1	13	-14	-3	1	1	58	59	2	1	1	76	-79
4	4	0	17	18	11	2	0	14	-15	-9	1	1	14	14	-3	2	1	25	24	3	0	1	26	-26
4	5	0	14	15	11	1	0	11	11	-9	2	1	17	18	-3	4	1	26	-27	3	1	1	46	-46
4	6	0	6	-7	12	0	0	15	-15	-9	5	1	8	8	-3	5	1	10	-9	3	2	1	5	7
4	7	0	7	8	12	1	0	13	12	-9	6	1	11	-8	-2	8	1	7	5	3	3	1	5	5
5	7	0	6	5	13	5	0	7	6	-9	7	1	7	-3	-2	6	1	15	15	3	4	1	19	-19
5	5	0	11	11	13	4	0	10	9	-8	7	1	8	-7	-2	4	1	19	19	3	5	1	11	12
5	4	0	7	-7	13	2	0	8	9	-8	6	1	8	8	-2	3	1	25	-26	3	7	1	7	5
5	3	0	18	-18	14	0	0	11	11	-8	4	1	10	9	-2	2	1	76	-76	4	6	1	8	9
5	2	0	20	19	14	1	0	8	-10	-8	3	1	6	5	-2	1	1	44	43	4	5	1	5	-4
5	1	0	27	-27	14	3	0	7	-6	-7	0	1	61	-61	-1	1	1	15	-15	4	4	1	7	9

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	3	1	26	26	13	0	1	17	-17	-8	0	2	6	-3	-1	5	2	18	-17	4	5	2	9	9
4	2	1	58	-57	13	4	1	12	13	-8	1	2	18	-17	-1	4	2	27	26	4	6	2	6	-5
4	1	1	38	-37	14	2	1	6	2	-8	2	2	12	-12	-1	3	2	35	34	4	7	2	7	-6
5	0	1	95	-94	14	1	1	11	10	-8	3	2	8	-6	-1	2	2	92	90	5	5	2	9	-8
5	2	1	6	9	15	0	1	7	-6	-8	7	2	13	13	-1	1	2	91	92	5	4	2	30	-29
5	3	1	5	-4	15	3	1	7	-4	-7	6	2	8	-8	0	0	2	35	36	5	2	2	8	9
5	4	1	10	11	-16	0	2	8	-6	-7	5	2	7	8	0	1	2	5	4	6	1	2	7	-6
5	5	1	17	-16	-16	1	2	10	10	-7	4	2	15	-14	0	2	2	42	-43	6	2	2	31	-31
6	6	1	8	-9	-16	3	2	6	6	-7	3	2	8	-7	0	3	2	33	-33	6	3	2	16	-16
6	4	1	22	21	-15	3	2	7	-5	-7	1	2	11	-10	0	4	2	17	16	6	4	2	18	18
6	3	1	15	-14	-15	1	2	15	16	-6	0	2	9	9	0	5	2	12	-12	6	5	2	6	7
6	2	1	13	13	-14	1	2	20	-20	-6	3	2	12	12	0	7	2	7	9	6	6	2	14	14
6	1	1	33	-31	-14	2	2	14	14	-6	5	2	22	-22	1	5	2	14	14	7	4	2	17	18
7	1	1	14	-14	-14	3	2	19	-20	-6	7	2	6	-7	1	4	2	21	-20	7	3	2	29	28
7	2	1	52	51	-13	5	2	13	12	-5	6	2	8	9	1	3	2	19	-19	7	2	2	51	52
7	6	1	21	-20	-13	4	2	11	-11	-5	5	2	9	9	1	2	2	60	-61	8	0	2	77	74
8	5	1	7	7	-13	2	2	14	14	-5	4	2	26	-26	1	1	2	98	-101	8	1	2	41	42
8	4	1	11	-12	-13	1	2	19	-19	-5	3	2	5	6	2	0	2	18	18	8	2	2	6	7
8	1	1	29	28	-12	0	2	17	18	-5	1	2	18	17	2	1	2	26	25	8	4	2	12	-12
9	0	1	24	-24	-12	1	2	10	10	-4	0	2	29	29	2	2	2	54	-55	8	5	2	12	-13
9	1	1	13	-13	-12	3	2	36	37	-4	1	2	18	-19	2	4	2	21	-21	9	5	2	11	10
9	2	1	10	9	-12	4	2	18	-19	-4	2	2	17	-17	2	5	2	9	-10	9	4	2	11	-9
9	3	1	17	17	-12	5	2	6	5	-4	3	2	34	35	2	6	2	17	-17	9	2	2	21	-21
9	4	1	8	8	-11	5	2	13	-13	-4	4	2	12	13	2	8	2	7	4	9	1	2	24	-23
9	6	1	6	4	-11	4	2	9	-10	-4	5	2	9	8	3	6	2	7	8	10	0	2	8	-7
9	7	1	7	-8	-11	2	2	7	7	-3	7	2	6	1	3	5	2	7	-7	10	1	2	13	14
10	4	1	6	-9	-10	0	2	13	13	-3	5	2	14	-13	3	4	2	6	4	11	5	2	10	-9
10	1	1	10	-10	-10	2	2	6	-9	-3	4	2	24	-24	3	3	2	28	-29	11	3	2	16	-18
11	0	1	9	11	-10	3	2	9	9	-3	2	2	59	60	3	2	2	53	54	11	2	2	14	15
11	1	1	11	-11	-10	5	2	8	-8	-3	1	2	29	29	3	1	2	31	30	11	1	2	14	15
12	6	1	8	9	-10	6	2	10	9	-2	0	2	71	72	4	0	2	62	61	12	0	2	8	9
12	3	1	10	9	-9	5	2	9	-9	-2	2	2	55	-53	4	1	2	19	-19	12	1	2	14	-12
12	2	1	19	-18	-9	2	2	8	9	-2	3	2	22	21	4	3	2	5	-3	12	3	2	11	-8
12	1	1	8	-7	-9	1	2	11	11	-2	6	2	12	12	4	4	2	5	4	13	4	2	8	-9

K	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
13	3	2	7	6	-6	2	3	37	-38	2	5	3	13	-15	8	5	3	11	9	-10	0	4	7	9
14	3	2	9	10	-6	1	3	35	-35	2	4	3	25	24	8	3	3	6	5	-10	2	4	12	12
15	3	2	6	2	-5	0	3	7	-7	2	3	3	15	-14	8	2	3	18	17	-10	5	4	9	-11
16	0	2	7	-7	-5	1	3	40	40	2	2	3	4	-2	8	1	3	11	-12	-9	5	4	6	5
-17	1	3	9	-9	-5	2	3	21	21	3	0	3	44	-43	9	0	3	9	6	-9	1	4	5	-6
-16	3	3	7	9	-5	3	3	13	12	3	1	3	9	-9	9	1	3	27	-25	-8	2	4	11	12
-15	0	3	17	17	-5	5	3	16	16	3	2	3	15	14	9	2	3	6	-6	-8	3	4	15	16
-14	2	3	13	-14	-4	4	3	23	23	3	3	3	7	6	9	3	3	16	-17	-8	4	4	8	7
-13	1	3	8	10	-4	3	3	19	-18	3	5	3	11	10	9	4	3	11	-11	-8	5	4	7	-9
-13	2	3	10	-9	-4	2	3	19	-20	3	6	3	8	7	10	6	3	7	7	-8	6	4	6	-7
-12	4	3	16	17	-4	1	3	12	12	3	7	3	10	10	10	4	3	14	14	-8	7	4	7	-4
-12	3	3	12	-13	-3	0	3	87	-89	4	5	3	20	20	10	2	3	5	-3	-7	6	4	7	-5
-12	2	3	7	4	-3	1	3	35	35	4	4	3	21	19	10	1	3	11	-12	-7	5	4	7	-7
-12	1	3	21	-20	-3	2	3	13	13	4	3	3	21	20	11	0	3	14	14	-7	4	4	15	-13
-11	0	3	7	-8	-3	5	3	5	3	4	2	3	27	-27	11	1	3	10	12	-7	2	4	24	24
-11	1	3	7	8	-2	5	3	12	12	4	1	3	7	8	11	3	3	12	14	-7	1	4	35	34
-11	5	3	9	6	-2	4	3	12	12	5	0	3	23	-23	12	1	3	11	9	-6	0	4	19	19
-10	2	3	6	-6	-2	1	3	35	34	5	1	3	10	9	13	2	3	6	5	-6	1	4	53	-52
-10	1	3	7	5	-1	0	3	45	-46	5	2	3	19	18	13	3	3	6	-5	-6	3	4	17	-17
-9	0	3	13	13	-1	2	3	20	21	5	3	3	13	13	13	4	3	8	6	-6	7	4	8	9
-9	1	3	6	6	-1	3	3	19	20	5	4	3	6	-7	15	0	3	7	-5	-5	7	4	7	4
-9	5	3	11	11	-1	5	3	11	11	5	5	3	13	-13	16	2	3	6	-3	-5	6	4	6	9
-8	5	3	15	-15	-1	6	3	7	9	5	6	3	7	-4	-16	0	4	14	-14	-5	5	4	13	12
-8	2	3	26	-28	0	5	3	11	-10	6	6	3	11	12	-16	2	4	8	7	-5	3	4	10	10
-8	1	3	15	14	0	4	3	11	-10	6	4	3	9	10	-15	1	4	8	9	-5	2	4	35	34
-7	0	3	19	19	0	3	3	21	-21	6	3	3	11	-12	-14	0	4	15	-14	-5	1	4	63	-62
-7	1	3	12	-12	0	2	3	69	-69	6	2	3	32	-33	-14	1	4	8	-8	-4	1	4	29	29
-7	2	3	7	7	0	1	3	5	5	6	1	3	39	38	-13	2	4	26	26	-4	2	4	21	-20
-7	3	3	42	-43	1	0	3	22	-22	7	0	3	7	-37	-13	1	4	19	-18	-4	3	4	45	44
-7	6	3	6	4	1	1	3	63	-62	7	1	3	24	-24	-12	0	4	6	7	-4	6	4	8	7
-6	6	3	7	-5	1	2	3	21	-19	7	2	3	13	14	-12	3	4	6	6	-3	5	4	6	-4
6	5	3	18	19	1	3	3	49	-47	7	4	3	20	20	-12	4	4	8	-7	-3	4	4	24	-25
-6	4	3	10	10	1	4	3	38	-39	7	7	3	6	3	-11	3	4	9	11	-3	3	4	12	12
6	3	3	26	26	1	5	3	9	9	8	0	3	9	12	-11	1	4	6	4	-3	2	4	10	19

TABLE 6 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	1	4	22	-23	3	1	4	21	21	15	2	4	6	-4	-4	3	5	8	-6	3	2	5	20	19
-2	0	4	22	-22	4	1	4	8	-7	-15	0	5	7	5	-4	2	5	7	-5	3	3	5	7	-17
-2	1	4	22	22	4	2	4	9	8	-15	1	5	7	4	-4	1	5	16	-15	3	4	5	5	-5
-2	2	4	13	-13	4	3	4	23	-21	-14	3	5	7	-3	-3	0	5	43	44	3	5	5	10	12
-2	3	4	15	15	4	4	4	22	22	-14	1	5	8	-8	-3	1	5	19	-19	3	7	5	11	11
-2	4	4	30	29	5	4	4	14	-15	-13	0	5	18	-18	-3	2	5	16	16	4	3	5	14	14
-1	6	4	8	-9	5	3	4	17	18	-13	1	5	7	9	-3	3	5	23	-23	4	2	5	31	-31
-1	4	4	7	-8	5	2	4	22	23	-13	2	5	17	-16	-3	4	5	15	-16	4	1	5	8	7
-1	3	4	13	-13	5	1	4	9	-9	-12	3	5	7	-5	-2	5	5	8	5	5	1	5	5	5
-1	2	4	47	47	6	0	4	6	-4	-12	2	5	7	-2	-2	4	5	8	8	5	2	5	11	-12
-1	1	4	5	4	6	1	4	17	17	-12	1	5	12	13	-2	2	5	11	-13	5	3	5	9	9
0	0	4	75	74	6	2	4	5	-4	-11	0	5	30	31	-2	1	5	13	-12	6	4	5	12	13
0	1	4	12	-12	6	3	4	6	8	-11	2	5	9	10	-1	0	5	25	26	6	3	5	5	-5
0	2	4	10	-11	7	3	4	8	10	-11	3	5	9	-9	-1	1	5	23	23	6	2	5	13	-13
0	3	4	24	-24	7	2	4	20	21	-10	1	5	11	12	-1	2	5	5	-2	7	1	5	9	9
0	4	4	27	-28	8	0	4	11	-9	-9	0	5	16	15	-1	3	5	5	5	7	2	5	8	-7
0	5	4	8	-9	8	3	4	18	-18	-9	2	5	10	-10	-1	4	5	18	-17	7	4	5	7	8
0	6	4	18	-19	8	5	4	12	-12	-9	3	5	14	-15	-1	5	5	12	-13	7	5	5	9	-6
1	7	4	7	-6	9	5	4	10	-9	-9	4	5	9	-10	0	6	5	8	-8	8	6	5	8	-8
1	6	4	7	-3	9	4	4	8	-5	-9	5	5	6	5	0	5	5	7	-8	8	5	5	8	-9
1	5	4	13	-13	9	3	4	12	-13	-8	4	5	9	7	0	3	5	18	-19	8	3	5	12	-12
1	4	4	24	-25	10	0	4	23	-22	-8	3	5	11	10	0	2	5	19	-20	8	2	5	8	-7
1	3	4	12	-11	10	1	4	10	9	-8	2	5	16	-15	0	1	5	10	11	8	1	5	14	14
1	2	4	9	9	10	2	4	8	-8	-7	1	5	18	17	1	0	5	6	-6	9	1	5	7	6
1	1	4	4	-2	10	3	4	15	15	-7	3	5	8	-6	1	1	5	21	20	9	2	5	18	-18
2	0	4	41	-41	10	5	4	7	7	-7	4	5	5	5	1	3	5	32	31	9	3	5	8	10
2	1	4	30	30	11	5	4	6	2	-6	4	5	17	16	1	5	5	7	3	9	4	5	15	-14
2	2	4	24	-24	11	2	4	18	19	-6	3	5	19	-19	2	7	5	11	9	10	4	5	11	10
2	3	4	36	37	12	0	4	11	9	-5	0	5	23	-23	2	4	5	11	11	11	0	5	16	17
2	4	4	16	17	12	1	4	7	-10	-5	1	5	8	7	2	3	5	9	-9	11	3	5	7	-8
2	5	4	10	11	12	2	4	7	8	-5	2	5	11	-10	2	2	5	17	-18	12	2	5	13	-12
2	6	4	7	7	12	3	4	11	-11	-5	3	5	6	-5	2	1	5	17	16	12	1	5	13	16
3	6	4	13	15	13	2	4	6	5	-5	4	5	9	-9	3	0	5	65	63	13	2	5	7	-6
3	3	4	23	24	13	1	4	8	-7	-4	7	5	7	-5	3	1	5	40	-40	13	3	5	9	-8

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
14	3	5	6	-1	-3	5	6	7	-7	2	6	6	6	6	14	0	6	9	-6	-3	5	7	12	-14
15	0	5	7	6	-3	4	6	6	-7	3	5	6	14	-14	14	1	6	9	-12	-3	6	7	12	11
15	1	5	8	8	-3	2	6	5	5	3	3	6	6	-6	15	3	6	8	9	-2	5	7	10	11
-16	0	6	7	-6	-3	1	6	39	38	3	2	6	7	8	15	1	6	11	-8	-2	4	7	7	-7
-14	0	6	22	-22	-2	0	6	42	-44	3	1	6	55	55	-15	0	7	10	11	-2	2	7	6	-5
-14	1	6	6	-6	-2	1	6	9	-9	4	0	6	19	-19	-14	1	7	9	-7	-1	0	7	10	-10
-12	0	6	9	10	-2	2	6	7	-6	4	1	6	14	-13	-13	0	7	14	14	-1	2	7	7	-5
-12	2	6	13	12	-2	3	6	6	-3	4	2	6	22	22	-13	1	7	13	12	-1	5	7	9	-6
-12	3	6	10	10	-2	4	6	21	21	4	3	6	13	-15	-13	3	7	8	5	0	5	7	8	-5
-11	3	6	11	12	-2	5	6	7	-6	4	4	6	10	-13	-12	1	7	14	14	0	4	7	12	13
-11	2	6	7	10	-2	6	6	7	8	5	4	6	7	2	-11	1	7	10	8	0	3	7	17	-16
-11	1	6	13	14	-2	7	6	10	-9	5	4	6	14	-14	-11	4	7	11	11	0	2	7	28	28
-10	0	6	11	-11	-1	6	6	11	-10	5	1	6	26	-25	-10	3	7	6	-7	0	1	7	14	13
-10	5	6	10	-8	-1	3	6	5	5	6	0	6	37	-38	-9	0	7	13	12	1	0	7	58	56
-9	3	6	7	-7	-1	2	6	45	44	6	1	6	7	-8	-9	1	7	8	6	1	1	7	27	-26
-9	2	6	7	-7	-1	1	6	9	-8	6	5	6	8	8	-9	4	7	15	-16	1	3	7	13	-13
-8	0	6	17	-17	0	0	6	37	37	7	4	6	10	-10	-8	6	7	8	5	1	4	7	17	-17
-8	1	6	14	-14	0	1	6	16	-16	7	3	6	15	14	-7	1	7	6	5	1	7	7	9	7
-8	3	6	6	4	0	2	6	10	10	7	2	6	11	10	-7	2	7	7	-7	2	3	7	8	8
-7	4	6	6	-3	0	3	6	17	-17	7	1	6	14	-15	-7	4	7	8	-7	2	2	7	11	-8
-6	0	6	41	-40	0	4	6	13	-12	8	1	6	8	8	-6	5	7	9	-7	3	0	7	24	24
-6	1	6	16	-17	0	5	6	7	6	8	3	6	6	8	-6	4	7	6	-4	3	1	7	12	11
-6	2	6	16	-16	0	6	6	12	-12	8	4	6	9	-10	-6	2	7	10	-11	3	2	7	12	-13
-6	4	6	5	4	1	6	6	12	13	9	3	6	7	-3	-6	1	7	8	-7	3	3	7	20	20
-5	5	6	10	6	1	5	6	22	23	9	1	6	17	-18	-5	0	7	6	-3	3	4	7	6	8
-5	4	6	6	5	1	4	6	6	-6	10	0	6	13	-14	-5	2	7	8	-7	4	6	7	7	-5
-5	3	6	8	8	1	3	6	19	19	10	2	6	10	11	-4	4	7	10	10	4	4	7	7	7
-5	2	6	13	12	1	2	6	28	-27	11	2	6	9	-8	-4	3	7	10	10	4	1	7	11	-10
-5	1	6	36	-36	1	1	6	57	-56	11	1	6	27	29	-4	2	7	14	14	5	0	7	9	10
-4	0	6	13	11	2	0	6	7	-6	12	0	6	10	-10	-4	1	7	27	25	5	1	7	7	6
-4	2	6	14	15	2	1	6	25	24	12	1	6	10	-9	-3	0	7	16	15	5	2	7	20	-19
-4	3	6	9	8	2	2	6	15	16	12	2	6	11	9	-3	1	7	21	20	5	4	7	8	-9
-4	5	6	6	-3	2	3	6	16	16	13	3	6	6	-4	-3	2	7	6	5	5	5	7	11	-11
-4	6	6	16	-16	2	4	6	14	14	13	2	6	8	8	-3	3	7	7	8	6	5	7	6	3

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	3	7	8	-9	-6	0	8	6	-6	4	0	8	36	-36	-11	4	9	7	-8	0	3	9	8	9
6	2	7	7	-6	-6	1	8	12	-14	4	1	8	17	-18	-10	4	9	8	-7	0	2	9	8	8
7	0	7	14	15	-5	6	8	7	7	4	2	8	5	3	-10	3	9	7	-9	1	0	9	13	13
7	3	7	6	-5	-5	4	8	6	-2	4	3	8	13	-12	-9	5	9	9	7	1	2	9	10	-9
7	6	7	7	-8	-4	2	8	7	8	5	4	8	12	-12	-8	5	9	7	-3	1	3	9	6	3
8	5	7	7	6	-4	3	8	14	12	5	1	8	8	-8	-8	2	9	8	4	1	4	9	7	7
8	3	7	7	-9	-4	4	8	15	16	6	0	8	26	-26	-7	0	9	7	7	1	5	9	9	-9
8	2	7	6	5	-4	5	8	6	6	6	2	8	7	4	-7	3	9	9	-9	2	2	9	6	4
8	1	7	13	-14	-3	6	8	6	-8	6	4	8	11	11	-6	4	9	6	8	3	0	9	10	10
9	2	7	13	-13	-3	5	8	8	9	6	6	8	10	12	-6	3	9	7	7	3	2	9	9	-10
9	3	7	9	9	-3	4	8	13	-13	7	5	8	7	-8	-6	2	9	7	7	3	3	9	7	-8
10	3	7	10	10	-3	3	8	19	20	7	4	8	18	19	-6	1	9	12	-12	5	0	9	10	10
10	1	7	16	16	-3	2	8	11	-12	7	3	8	7	5	-5	0	9	19	19	5	5	9	7	-7
11	0	7	47	47	-3	1	8	7	-7	7	2	8	20	20	-5	1	9	20	20	6	4	9	9	-8
11	1	7	6	6	-2	0	8	14	-15	7	1	8	9	9	-5	2	9	15	16	6	2	9	8	-7
12	2	7	9	-11	-2	2	8	10	-8	8	0	8	9	10	-5	3	9	16	14	7	0	9	17	-19
12	1	7	9	-8	-2	3	8	8	-10	8	2	8	12	13	-4	5	9	7	8	7	2	9	14	-15
13	0	7	8	-9	-1	6	8	7	6	8	3	8	15	-14	-4	4	9	13	-14	7	3	9	10	10
13	1	7	13	13	-1	5	8	17	-16	8	4	8	18	-20	-4	2	9	18	-18	7	4	9	19	19
13	2	7	12	-12	-1	4	8	16	16	9	5	8	16	15	-4	1	9	10	9	8	5	9	8	-7
14	3	7	9	-7	-1	3	8	7	-9	9	2	8	26	-25	-3	0	9	23	-24	8	2	9	35	35
14	1	7	10	5	-1	1	8	13	15	9	1	8	9	-9	-3	1	9	14	-14	9	0	9	46	46
-14	1	8	7	-8	0	0	8	23	-22	10	0	8	13	-13	-3	3	9	9	-10	9	3	9	8	-7
-13	2	8	10	12	0	3	8	10	-10	10	1	8	7	9	-3	4	9	11	13	9	4	9	9	-10
-12	1	8	8	13	1	4	8	8	10	10	2	8	21	21	-2	5	9	8	-7	10	3	9	10	12
-12	3	8	9	9	1	3	8	7	-8	10	3	8	19	19	-2	4	9	6	-5	10	1	9	7	-7
-11	4	8	7	-7	1	2	8	9	8	10	4	8	9	8	-2	3	9	10	-9	11	1	9	13	11
-11	2	8	17	-18	2	2	8	20	18	11	3	8	10	-10	-2	2	9	22	22	11	2	9	9	-10
-10	0	8	8	-8	2	4	8	8	-9	11	2	8	10	11	-1	0	9	10	10	12	2	9	12	-12
-10	5	8	7	-5	2	6	8	10	-9	11	1	8	14	15	-1	2	9	16	-16	13	1	9	7	5
-9	4	8	8	10	3	6	8	9	10	12	0	8	18	-18	-1	3	9	27	28	-12	0	10	7	5
-9	1	8	6	-5	3	5	8	7	4	12	1	8	19	-20	-1	4	9	17	-17	-9	3	10	8	-5
-8	1	8	6	1	3	2	8	16	-16	12	3	8	10	-8	-1	5	9	8	8	-9	2	10	8	-9
-7	2	8	6	-6	3	1	8	7	-7	13	1	8	12	-11	0	4	9	7	-5	-8	2	10	8	6

TABLE 6 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-8	4	10	7	6	0	2	10	13	13	-7	1	11	11	10	5	2	11	7	-5	5	2	12	7	-10
-7	3	10	9	-8	0	3	10	15	-13	-6	3	11	8	-8	6	2	11	11	13	6	0	12	18	-19
-7	1	10	20	20	1	5	10	7	8	-6	1	11	11	11	6	1	11	12	-13	6	3	12	7	3
-6	1	10	24	-23	2	4	10	8	-8	-5	0	11	20	-20	7	0	11	7	9	-7	0	13	12	-10
-6	2	10	7	-5	3	5	10	7	-8	-5	1	11	15	-16	7	2	11	7	-9	-5	0	13	13	-11
-6	3	10	19	-20	3	2	10	12	-10	-5	2	11	6	7	8	2	11	7	-6	-5	1	13	8	-4
-6	4	10	12	-11	3	1	10	7	7	-5	3	11	12	-13	8	1	11	7	5	-3	0	13	10	-7
-5	5	10	14	14	5	3	10	7	7	-5	4	11	8	8	10	1	11	7	-4	-3	1	13	9	-9
-5	4	10	9	9	5	2	10	8	-7	-4	2	11	16	16	-9	1	12	9	10	-1	0	13	17	16
-5	3	10	16	17	6	1	10	10	13	-4	1	11	11	-10	-8	0	12	7	7	-1	2	13	10	10
-5	2	10	20	20	6	2	10	7	5	-3	3	11	14	16	-6	2	12	13	-12	0	3	13	6	6
-5	1	10	23	-23	6	4	10	7	-10	-3	4	11	10	-10	-4	1	12	8	4	1	0	13	14	-14
-4	0	10	47	48	6	5	10	8	8	-2	2	11	15	14	-4	2	12	7	-3	1	3	13	8	7
-4	1	10	9	10	7	5	10	7	-2	-2	1	11	25	-25	-4	3	12	9	-11	2	3	13	10	-9
-4	2	10	8	7	7	4	10	8	6	-1	0	11	8	8	-3	1	12	17	-17	3	1	13	14	-14
-4	4	10	12	-12	7	2	10	13	-13	0	3	11	10	11	-2	0	12	16	-16	4	3	13	7	2
-3	5	10	11	-11	7	1	10	9	8	0	2	11	13	-12	-1	3	12	6	0	4	1	13	8	-5
-3	2	10	37	-37	8	0	10	29	-29	0	1	11	15	16	-1	1	12	18	18	6	1	13	8	-7
-2	0	10	30	-30	8	4	10	8	7	1	5	11	7	-7	0	0	12	23	24	7	0	13	8	6
-2	1	10	24	24	9	4	10	10	7	2	3	11	6	-5	0	2	12	12	12	-2	1	14	9	8
-2	2	10	13	-16	9	2	10	12	14	2	2	11	9	6	2	3	12	10	-10	-1	1	14	9	7
-2	3	10	11	11	10	2	10	7	7	3	2	11	6	5	3	4	12	10	9	1	2	14	7	-7
-1	4	10	12	14	11	2	10	9	-8	3	3	11	7	6	3	3	12	8	6	1	1	14	7	-8
-1	3	10	15	-17	-11	0	11	10	-9	4	4	11	9	-9	5	3	12	9	-9	2	1	14	7	6
-1	2	10	7	8	-8	3	11	11	11	5	1	11	10	-11										

TABLE 7 : FRACTIONAL ATOMIC COORDINATES (x 10^4) OF THE NON-HYDROGEN ATOMS FOR MODEL A AND MODEL B WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Model A			Model B		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
N(1)	1925(2)	6098(5)	6856(3)	1922(3)	6102(5)	6860(3)
N(2)	1242(2)	6730(5)	6507(3)	1241(3)	6731(6)	6507(3)
N(3)	335(3)	7445(7)	5220(4)	334(3)	7443(7)	5219(4)
N(4)	1587(3)	6269(5)	4737(3)	1586(3)	6269(6)	4736(3)
N(5)	2316(3)	5650(5)	4919(3)	2314(3)	5653(6)	4916(4)
O(1)	64(2)	6996(6)	4395(3)	64(2)	6995(6)	4396(3)
O(2)	-21(2)	8414(6)	5808(3)	-22(3)	8411(6)	5807(3)
C(3)	1150(3)	6752(7)	5511(4)	1149(3)	6751(7)	5511(5)
C(11)	1994(3)	6040(6)	7912(4)	1996(4)	6042(7)	7914(4)
C(12)	1317(4)	5932(7)	8549(4)	1318(4)	5932(7)	8546(4)
C(13)	1470(4)	5931(8)	9568(5)	1471(5)	5928(8)	9564(5)
C(14)	2248(8)	5984(8)	9943(5)	2250(5)	5984(8)	9943(5)
C(15)	2911(4)	6038(7)	9324(4)	2913(4)	6037(8)	9321(5)
C(16)	2790(3)	6043(7)	8299(4)	2797(4)	6042(7)	8296(4)
C(17)	446(3)	5715(8)	8186(4)	445(3)	5706(8)	8185(4)
C(18)	3518(3)	6111(7)	7630(4)	3520(3)	6135(8)	7631(4)
C(51)	2780(3)	5120(6)	4072(4)	2781(4)	5119(7)	4070(4)
C(52)	2412(3)	4371(7)	3224(4)	2412(4)	4368(7)	3224(4)
C(53)	2938(5)	3853(7)	2458(4)	2939(4)	3850(8)	2458(5)
C(54)	3768(4)	4090(8)	2519(5)	3768(4)	4089(9)	2519(5)
C(55)	4107(4)	4833(8)	3366(5)	4108(4)	4832(8)	3365(5)
C(56)	3618(4)	5369(7)	4156(4)	3619(4)	5373(7)	4155(4)
C(57)	1525(3)	3982(7)	3104(4)	1523(3)	3981(7)	3106(4)
C(58)	3998(3)	6187(7)	5064(4)	3998(3)	6192(8)	5067(4)

TABLE 8 : FRACTIONAL ATOMIC COORDINATES (x 10^3) OF THE HYDROGEN ATOMS[a] FOR MODEL A AND MODEL B

	Model A			Model B		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
H(13)	96	588	1007	97	588	1007
H(14)	235	599	1074	235	599	1074
H(15)	352	608	964	352	608	963
H(171)	41	481	756	42	481	756
H(172)	21	700	796	20	699	796
H(173)	8	520	878	8	517	878
H(181)	348	729	717	346	721	710
H(182)	353	494	716	367	490	724
H(183)	407	615	807	414	563	832
H(53)	268	326	179	268	326	179
H(54)	415	368	192	415	368	192
H(55)	475	502	342	476	501	342
H(571)	129	333	376	129	333	376
H(572)	146	311	247	145	311	247
H(573)	118	519	297	119	520	297
H(581)	462	657	491	462	658	492
H(582)	400	522	566	399	522	566
H(583)	366	735	530	366	735	530
H(N1/N5)[b]	249	570	602	-	-	-
H(N1)[c]	-	-	-	240	565	638
H(N5)[d]	-	-	-	256	556	566

[a] Numbered according to the atom to which bonded.

[b] Site occupancy factor (s.o.f.) = 1.0; constrained to be equidistant from N(1) and N(5).

[c] S.o.f. = 0.55(7); calculated position.

[d] S.o.f. = 0.45(7); calculated position.

TABLE 9 : ANISOTROPIC THERMAL-MOTION PARAMETERS ($Å^2 \times 10^3$)[a] FOR MODEL A AND MODEL B WITH E.S.D.'S IN PARENTHESES

	Model A						Model B					
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	50(3)	52(3)	46(3)	1(2)	-6(2)	-1(3)	50(3)	51(3)	50(3)	-1(3)	-3(3)	0(3)
N(2)	49(3)	48(3)	49(3)	3(3)	-7(2)	-2(2)	47(3)	49(3)	51(3)	4(3)	-8(2)	-1(3)
N(3)	50(4)	78(4)	65(4)	17(3)	3(3)	-4(3)	49(4)	79(4)	66(4)	17(4)	2(3)	-2(3)
N(4)	47(3)	55(3)	56(3)	4(2)	2(2)	0(3)	47(3)	55(3)	57(3)	3(3)	1(3)	1(3)
N(5)	47(3)	54(3)	54(3)	4(3)	1(2)	5(3)	47(3)	56(3)	54(4)	6(3)	-1(3)	7(3)
O(1)	70(3)	130(4)	67(3)	9(3)	-23(2)	8(3)	69(3)	130(4)	66(3)	10(3)	-24(2)	9(3)
O(2)	65(3)	112(4)	84(3)	14(3)	11(2)	33(3)	65(3)	112(4)	84(3)	14(3)	10(3)	32(3)
C(3)	33(3)	58(4)	54(4)	9(3)	-2(3)	1(3)	34(4)	58(4)	52(4)	9(4)	-2(3)	0(3)
C(11)	67(4)	38(4)	50(4)	-2(3)	-1(3)	4(4)	72(4)	38(4)	44(4)	-1(3)	0(4)	4(4)
C(12)	74(4)	51(4)	61(4)	1(4)	-2(4)	6(4)	77(5)	50(4)	60(4)	2(4)	-2(4)	8(4)
C(13)	116(6)	70(4)	53(4)	0(4)	14(4)	9(5)	117(6)	71(5)	54(5)	0(4)	16(4)	9(5)
C(14)	138(6)	63(4)	46(4)	0(4)	-11(5)	4(5)	138(7)	62(5)	47(5)	-1(4)	-14(5)	3(6)
C(15)	100(5)	52(4)	63(4)	-5(4)	-23(4)	-7(4)	97(6)	53(4)	65(5)	-6(4)	-20(4)	-6(4)
C(16)	70(4)	46(4)	48(4)	1(3)	-12(3)	-4(4)	71(4)	47(4)	47(4)	1(3)	-15(4)	-4(4)
C(17)	76(5)	106(5)	71(4)	6(4)	20(4)	7(4)	72(5)	105(6)	74(5)	9(4)	20(4)	10(5)
C(18)	58(4)	80(4)	75(4)	5(4)	-11(3)	-11(4)	60(4)	78(5)	68(4)	14(4)	-3(4)	0(4)
C(51)	58(4)	40(4)	48(4)	1(3)	-1(3)	2(3)	60(4)	40(4)	46(4)	0(3)	0(4)	4(3)
C(52)	65(4)	44(4)	61(4)	-3(3)	-5(4)	-5(4)	67(4)	45(4)	60(4)	-4(4)	-5(4)	-6(4)
C(53)	101(5)	60(4)	49(4)	-7(3)	3(4)	8(4)	103(5)	59(4)	49(4)	-5(4)	2(4)	9(5)
C(54)	98(6)	80(5)	64(5)	-6(4)	17(4)	19(5)	96(6)	78(5)	65(5)	-6(4)	18(4)	16(5)
C(55)	70(4)	69(4)	61(4)	5(4)	15(4)	15(4)	72(5)	69(5)	61(4)	5(4)	15(4)	17(4)
C(56)	60(4)	49(4)	56(4)	-1(3)	-5(3)	7(3)	58(4)	49(4)	58(4)	1(3)	-5(4)	7(4)
C(57)	84(5)	76(4)	86(5)	-21(4)	-11(4)	-20(4)	81(5)	80(5)	87(5)	-20(4)	-11(4)	-17(4)
C(58)	56(4)	91(5)	77(4)	-11(4)	0(3)	8(4)	55(4)	91(5)	77(5)	-11(4)	-1(4)	6(4)

[a] In the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$

TABLE 10 : BOND LENGTHS (Å) FOR MODEL A AND MODEL B WITH E.S.D.'S IN PARENTHESES

	Model A	Model B
C(11) - C(12)	1.414(6)	1.411(6)
C(12) - C(13)	1.390(6)	1.388(7)
C(13) - C(14)	1.368(7)	1.372(8)
C(14) - C(15)	1.379(7)	1.381(7)
C(15) - C(16)	1.390(6)	1.389(6)
C(16) - C(11)	1.401(6)	1.406(7)
C(12) - C(17)	1.514(6)	1.517(6)
C(16) - C(18)	1.505(6)	1.496(7)
C(11) - N(1)	1.423(5)	1.421(6)
N(1) - N(2)	1.300(4)	1.298(5)
N(2) - C(3)	1.346(5)	1.346(6)
C(3) - N(3)	1.484(6)	1.484(6)
N(3) - O(1)	1.237(5)	1.234(5)
N(3) - O(2)	1.227(5)	1.226(5)
C(3) - N(4)	1.322(6)	1.322(6)
N(4) - N(5)	1.304(5)	1.301(5)
N(5) - C(51)	1.434(5)	1.436(6)
C(51) - C(52)	1.401(6)	1.400(6)
C(52) - C(53)	1.407(6)	1.408(7)
C(53) - C(54)	1.376(7)	1.374(7)
C(54) - C(55)	1.379(7)	1.378(7)
C(55) - C(56)	1.398(6)	1.399(7)
C(56) - C(51)	1.392(6)	1.392(7)
C(52) - C(57)	1.492(6)	1.495(6)
C(56) - C(58)	1.496(6)	1.500(6)

TABLE 11 : BOND ANGLES (°) FOR MODEL A AND MODEL B WITH E.S.D.'S IN PARENTHESES

	Model A	Model B
C(11) - C(12) - C(13)	117.6(5)	117.3(6)
C(12) - C(13) - C(14)	121.3(6)	121.5(7)
C(13) - C(14) - C(15)	121.3(6)	120.9(7)
C(14) - C(15) - C(16)	119.6(6)	120.1(6)
C(15) - C(16) - C(11)	119.3(5)	118.6(6)
C(16) - C(11) - C(12)	120.8(5)	121.4(5)
C(11) - C(12) - C(17)	123.9(5)	124.3(5)
C(13) - C(12) - C(17)	118.4(6)	118.3(6)
C(11) - C(16) - C(18)	121.5(5)	121.8(5)
C(15) - C(16) - C(18)	119.2(5)	119.5(6)
C(12) - C(11) - N(1)	123.5(5)	122.9(5)
C(16) - C(11) - N(1)	115.7(5)	115.6(5)
C(11) - N(1) - N(2)	115.4(4)	116.0(5)
N(1) - N(2) - C(3)	116.7(4)	117.0(5)
N(2) - C(3) - N(4)	136.4(5)	136.5(5)
N(2) - C(3) - N(3)	110.9(5)	110.9(5)
N(4) - C(3) - N(3)	112.6(5)	112.5(5)
C(3) - N(3) - O(1)	117.0(5)	117.1(6)
C(3) - N(3) - O(2)	118.2(5)	118.2(5)
O(1) - N(3) - O(2)	124.7(5)	124.8(6)
C(3) - N(4) - N(5)	117.1(4)	117.2(5)
N(4) - N(5) - C(51)	116.4(4)	116.7(5)
N(5) - C(51) - C(56)	115.6(5)	115.7(5)
N(5) - C(51) - C(52)	122.0(5)	121.7(5)
C(51) - C(52) - C(53)	116.3(5)	116.2(6)
C(52) - C(53) - C(54)	122.5(6)	122.5(6)
C(53) - C(54) - C(55)	119.4(6)	119.5(6)
C(54) - C(55) - C(56)	120.9(6)	120.9(6)
C(55) - C(56) - C(51)	118.4(5)	118.3(6)
C(56) - C(51) - C(52)	122.4(5)	122.6(6)
C(51) - C(52) - C(57)	125.2(5)	125.2(6)
C(53) - C(52) - C(57)	118.3(6)	118.5(6)
C(51) - C(56) - C(58)	121.6(5)	121.5(5)
C(55) - C(56) - C(58)	120.0(5)	120.2(6)

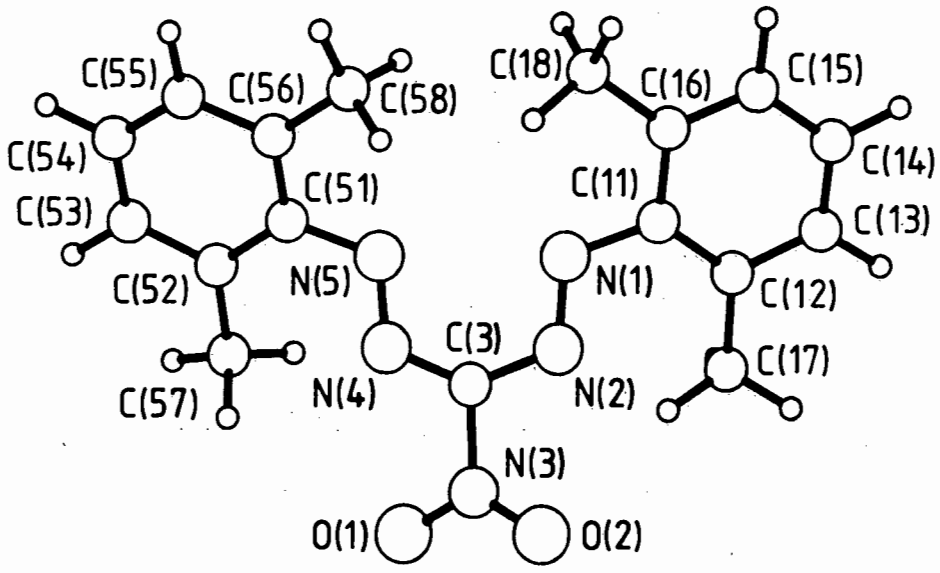


FIGURE 5 : The molecular structure and atomic nomenclature of the nitroformazan (14). Hydrogen atoms are numbered according to the atom to which they are bonded.

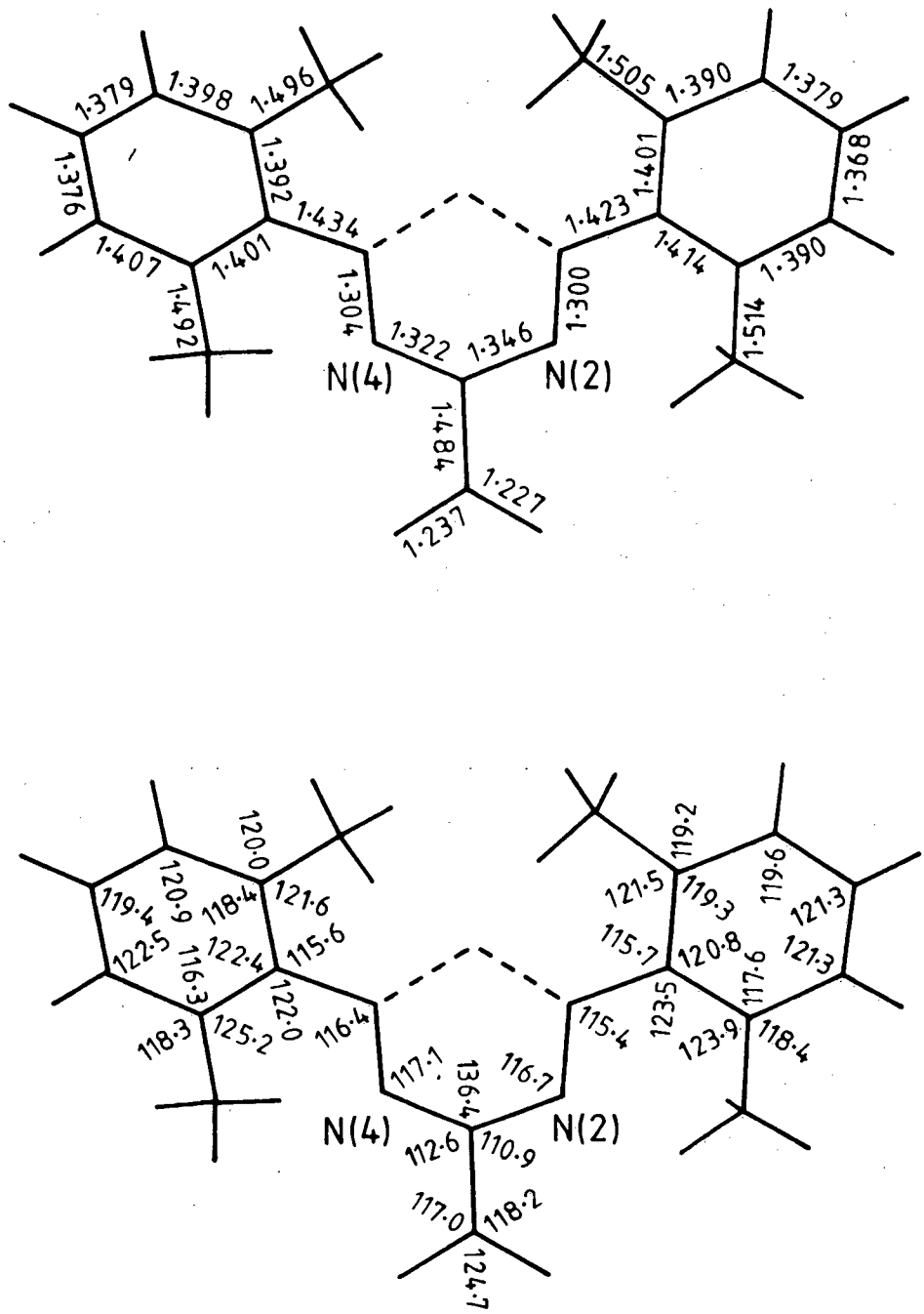


FIGURE 6 : Bond lengths (Å; upper molecule) and bond angles (Å; lower molecule) for Model A. E.s.d.'s are given in Tables 10 and 11.

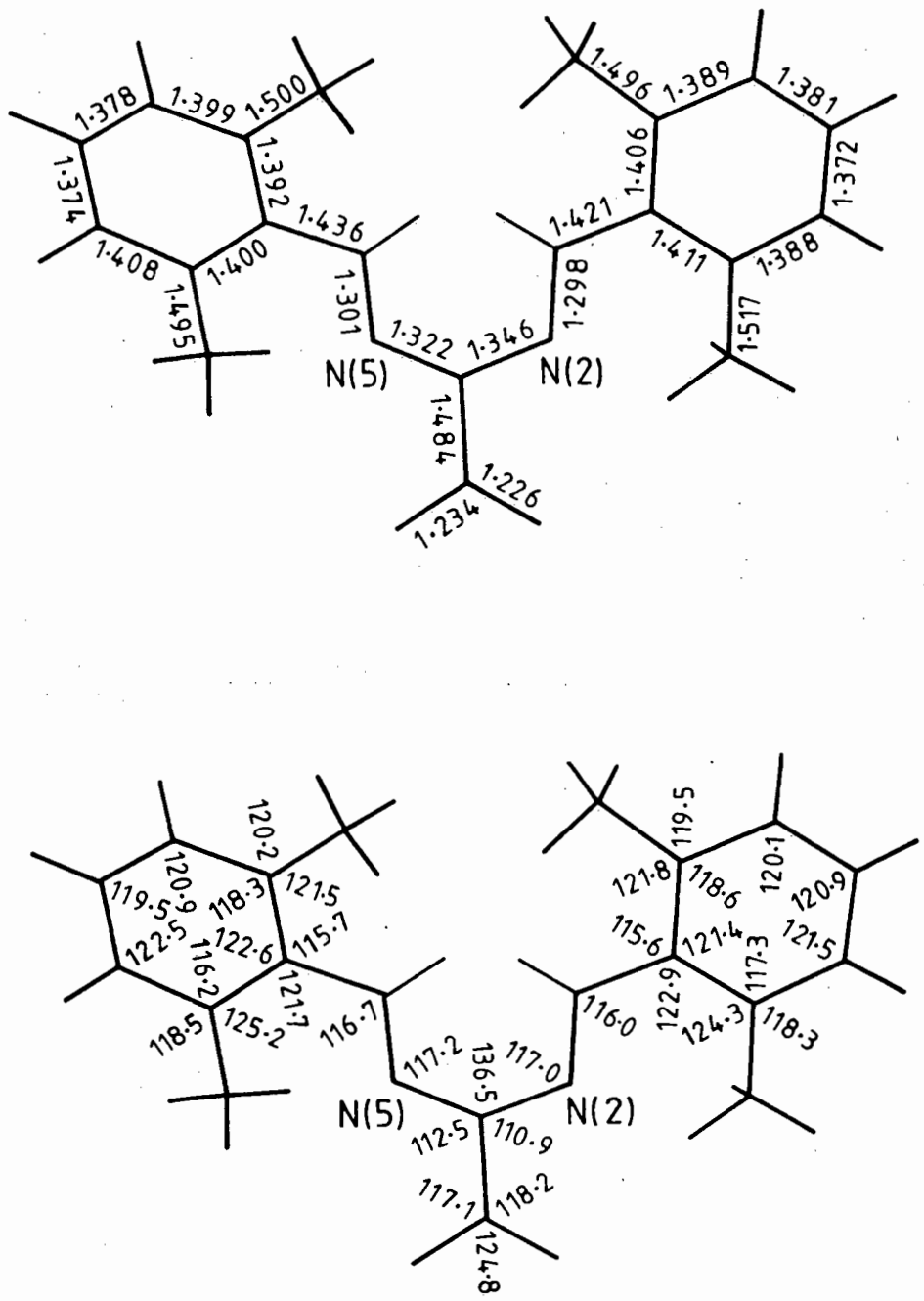


FIGURE 7 : Bond lengths (Å; upper molecule) and bond angles (Å; lower molecule) for Model B. E.s.d.'s are given in Tables 10 and 11.

The calculated bond lengths reveal virtually complete delocalization of π-electrons within the N-N-C-N-N chain. While the formal double bonds C(3)=N(4) (1.32 Å) and N(1)=N(2) (1.30 Å) are clearly extended in comparison with isolated double bonds, the formal single bonds C(3)-N(2) (1.35 Å) and N(4)-N(5) (1.30 Å) are obviously shortened. Accepted standard values for isolated C-N, C=N, N-N, and N=N bonds are 1.45, 1.27, 1.41, and 1.23 Å, respectively.[119-121] (The inability to locate the imino proton on *either* N(1) *or* N(5) has resulted in designation of *formal* double or single bonds based on the small difference in C-N lengths found in the formazan chain.) The two N-N distances are virtually identical, with bond orders of 1.58, while the two C-N distances within the formazan ring show bond orders of 1.47 [C(3)-N(2)] and 1.62 [C(3)-N(4)]. The bond orders used here correspond to 1 + *P*, where *P* is the double-bond character,[122,123] and were read off standard curves[121] of bond order *versus* bond length. The expected planarity of the N - N - C - N - N chain consequent on electron delocalization is confirmed by the torsion angles (ω) in the formazan chain (Table 12), where, for example, ω[N(1)-N(2)-C(3)-N(4)] is 0.0°. The parameters for some least-squares planes are listed in Table 13 where the deviations of atoms from the planes they define also show that the formazan chain is remarkably planar. The largest deviation of an atom in the chain from the N-N-C-N-N plane (Plane 2) is 0.02 Å, while the centered proton of Model A, H(N1/N5), deviates from this plane by 0.11 Å. Figure 8 illustrates this planarity and also shows that the aryl and nitro groups are somewhat twisted out of this plane.

Bond distances and angles relating to the aryl groups are generally satisfactory; the mean aromatic C-C distance in the two rings is 1.391 Å (Model A) or 1.392 Å (Model B), while the mean C-CH_3 distance is

TABLE 12 : SELECTED TORSION ANGLES (°)[a]

	Model A	Model B
C(11) - N(1) - N(2) - C(3)	-178.1[b]	-178.1[b]
N(2) - N(1) - C(11) - C(12)	25.7	25.7
N(2) - N(1) - C(11) - C(16)	-156.2	-156.2
N(1) - N(2) - C(3) - N(3)	178.0	178.0
N(1) - N(2) - C(3) - N(4)	0.0	0.0
O(1) - N(3) - C(3) - N(2)	-156.2	-156.3
O(1) - N(3) - C(3) - N(4)	21.9	21.9
O(2) - N(3) - C(3) - N(2)	23.7	23.6
O(2) - N(3) - C(3) - N(4)	-158.2	-158.2
C(3) - N(4) - N(5) - C(51)	180.0	180.0
N(5) - N(4) - C(3) - N(2)	-2.9	-2.8
N(5) - N(4) - C(3) - N(3)	180.0	180.0
N(4) - N(5) - C(51) - C(52)	-33.8	-33.8
N(4) - N(5) - C(51) - C(56)	147.3	147.2
N(1) - C(11) - C(12) - C(17)	5.2	5.5
N(1) - C(11) - C(12) - C(13)	-178.4	-178.4
C(16) - C(11) - C(12) - C(17)	-172.9	-172.5
N(1) - C(11) - C(16) - C(15)	178.2	178.2
N(1) - C(11) - C(16) - C(18)	0.0	1.1
C(12) - C(11) - C(16) - C(18)	178.4	180.0
C(17) - C(12) - C(13) - C(14)	174.9	174.8
C(18) - C(16) - C(15) - C(14)	180.0	178.8
N(5) - C(51) - C(52) - C(57)	-2.1	-2.1
N(5) - C(51) - C(52) - C(53)	-177.9	-178.1
C(56) - C(51) - C(52) - C(57)	176.8	176.9
N(5) - C(51) - C(56) - C(55)	178.3	178.3
N(5) - C(51) - C(56) - C(58)	-1.7	-1.3
C(52) - C(51) - C(56) - C(58)	180.0	180.0
C(57) - C(52) - C(53) - C(54)	-177.3	-177.4
C(58) - C(56) - C(55) - C(54)	180.0	180.0

[a] The torsion angle $\omega(I\text{-}J\text{-}K\text{-}L)$ is defined as the angle between the vector $J\text{-}I$ and the vector $K\text{-}L$ when viewed down $J\text{-}K$. The sign of ω is positive if $J\text{-}I$ is to be rotated clockwise into $K\text{-}L$ and negative if counterclockwise.[124]

Torsion angles within the aryl rings are all < 3.5° (Model A) or < 3.8° (Model B) and are omitted.

[b] Estimated standard deviations are *ca.* 0.6°.

TABLE 13 : LEAST-SQUARES PLANES PARAMETERS FOR MODEL A AND MODEL B

(a) Equations of least-squares planes for Model A and Model B expressed in orthogonalized space as

$PI + QJ + RK = S$

Plane 1 : all non-hydrogen atoms

Model A	$0.2210I + 0.9716J - 0.0849K$	$= 4.3419$
Model B	$0.2199I + 0.9718J - 0.0853K$	$= 4.3357$

Plane 2 : formazan chain: N(1), N(2), C(3), N(4), N(5)

Model A	$0.3871I + 0.9215J - 0.0316K$	$= 5.1553$
Model B	$0.3861I + 0.9219J - 0.0320K$	$= 5.1519$

Plane 3 : nitro group: C(3), N(3), O(1), O(2)

Model A	$0.4281I + 0.3118J - 0.4169K$	$= 1.7877$
Model B	$0.4279I + 0.8020J - 0.4166K$	$= 1.7894$

Plane 4 : aryl group (1): C(11) - C(18)

Model A	$-0.0512I + 0.9987J + 0.0005K$	$= 4.3034$
Model B	$-0.0541I + 0.9985J + 0.0029K$	$= 4.3212$

Plane 5 : aryl group (5): C(51) - C(58)

Model A	$-0.1047I + 0.9075J - 0.4067K$	$= 0.7889$
Model B	$-0.1051I + 0.9071J - 0.4076K$	$= 0.7812$

(b) Deviations (Å x 10^3) from planes for Model A and, in parentheses, Model B. Atoms included in the calculation are marked by asterisks. All e.s.d.'s are < 0.008 Å.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
N(1)	20 (20)*	-10 (-10)*	-596 (-596)	105 (102)	-704 (-706)
N(2)	271 (272)*	7 (8)*	-506 (-505)	635 (632)	28 (27)
N(3)	608 (609)*	-21 (-20)	0 (0)*	1246 (1241)	1367 (1366)
N(4)	262 (264)*	-16 (-16)*	454 (455)	260 (249)	626 (626)
N(5)	57 (58)*	12 (12)*	498 (501)	-264 (-276)	-14 (-11)
O(1)	276 (279)*	-468 (-466)	0 (0)*	932 (926)	1557 (1556)
O(2)	1116 (1118)*	397 (398)	0 (0)*	2002 (2000)	1763 (1760)
C(3)	367 (367)*	6 (6)*	0 (0)*	659 (652)	603 (601)
C(11)	-118 (-118)*	-51 (-50)	-1174(-1170)	56 (55)*	-1332(-1337)
C(12)	-516 (-516)*	-583 (-583)	-2077(-2072)	33 (35)*	-1643(-1647)
C(13)	-577 (-580)*	-530 (-533)	-2540(-2536)	20 (23)*	-2226(-2232)
C(14)	-298 (-301)*	-14 (-16)	-2165(-2161)	-5 (-3)*	-2523(-2530)
C(15)	54 (50)*	471 (468)	-1314(-1310)	-21 (-25)*	-2256(-2262)
C(16)	130 (129)*	441 (442)	-823 (-815)	-8 (-15)*	-1672(-1678)
C(17)	-950 (-956)*	-1272(-1278)	-2623(-2626)	-57 (-58)*	-1450(-1459)
C(18)	521 (535)*	980 (994)	111 (128)	-18 (-12)*	-1380(-1369)
C(51)	-64 (-64)*	-23 (-24)	984 (986)	-701 (-721)	12 (12)*
C(52)	-647 (-648)*	-738 (-741)	748 (746)	-1231(-1253)	27 (26)*
C(53)	-745 (-747)*	-729 (-732)	1240 (1238)	-1664(-1691)	7 (7)*
C(54)	-276 (-279)*	-40 (-43)	1938 (1937)	-1556(-1586)	-1 (0)*
C(55)	292 (289)*	653 (650)	2151 (2151)	-1028(-1056)	-14 (-15)*
C(56)	414 (415)*	679 (680)	1683 (1687)	-585 (-605)	-1 (1)*
C(57)	-1240(-1239)*	-1566(-1568)	-50 (-53)	-1448(-1464)	-27 (-26)*
C(58)	1044 (1044)*	1447 (1447)	1936 (1938)	-4 (-22)	-4 (-4)*

(c) Angles (°) between normals to planes. All e.s.d.'s are < 0.7°.

	Model A	Model B		Model A	Model B
Planes 1 and 2	10.4	10.4	Planes 2 and 4	25.8	25.9
Planes 1 and 3	24.6	24.6	Planes 2 and 5	36.0	36.0
Planes 1 and 4	16.5	16.6	Planes 3 and 4	38.9	39.1
Planes 1 and 5	26.7	26.7	Planes 3 and 5	31.5	31.5
Planes 2 and 3	23.4	23.4	Planes 4 and 5	24.3	24.5

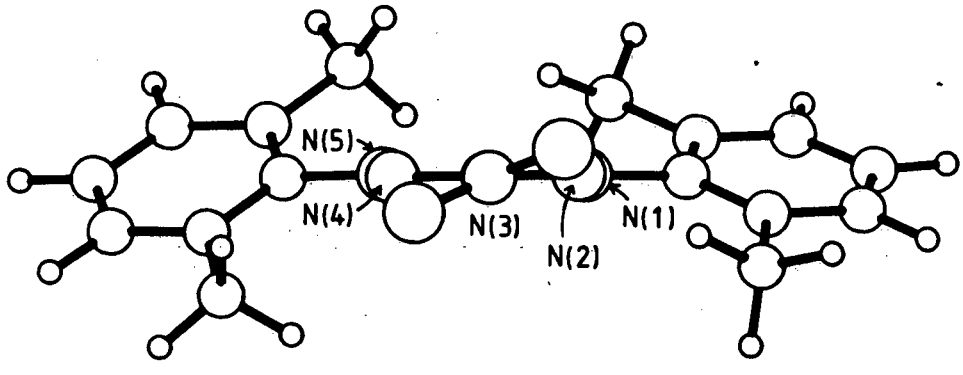


FIGURE 8 : View of the nitroformazan (14) down the N(3)-C(3) bond showing the planarity of the formazan ring and the twisting of the 2,6-dimethylphenyl groups out of this plane.

1.502 Å. Consideration of (Ar)C-N bond lengths shows that the aryl groups are essentially not conjugated with the formazan ring system (bond orders *ca.* 1.1); they are twisted out of its plane in similar senses, ring 1 by nearly 26° and ring 5 by 36° (Figure 8, Table 13). It is known that in related compounds, *e.g.*, 3-methythio-1,5-di(*o*-tolyl) formazan [(2f); $R^1 = R^2 =$ *o*-tolyl, $R^3 = SCH_3$], the delocalization in the N-N-C-N-N chain extends to the aryl groups to a much larger degree (reported in Chapter III of this thesis).[93,94] The methyl groups in the 2- and 6-positions on the aryl rings clearly result in the rings being twisted out of the N-N-C-N-N plane, resulting in diminished *p*-orbital interaction and a consequent decrease in π-electron delocalization. The effect of these non-bonded interactions (selected non-bonded distances are given in Table 14) is clearly seen by considering the aryl group attached to N(5) of the formazan ring. Although C(58) would remain at a constant distance from N(5) regardless of the degree of twisting of the aryl group, the C(57)···N(4) distance increases as ω[N(4)-N(5)-C(51)--C(52)] changes from 0°. (The torsion angle convention used is described in Table 12.) In this case ω changes to -34° and C(57)···N(4) increases to become equal to C(58)···N(5) at 2.79 Å. The exterior angles at C(51), however, show that the aryl group is further affected by the lone pair of electrons on N(4). This orbital is directed almost directly towards C(57), whereas the lone-pair orbital on N(5) is approximately parallel to the C(56)-C(58) bond, and this results in the bond angle N(5)-C(51)-C(52) (122°) being larger than N(5)-C(51)-(56) (116°). The exterior angles at C(52) (118° and 125°) show that the methyl group attached to this atom is repulsed to a larger extent than that attached to C(56) (120° and 122°), again as a result of the difference in orientation of the N(4) and N(5) lone-pair orbitals. Exactly analogous

TABLE 14 : INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) FOR MODEL A AND MODEL B

(a) Selected intramolecular non-bonded distances. E.s.d.'s are *ca.* 0.01 Å.

	Model A	Model B
N(1)···N(5)	2.71	2.72
N(1)···C(18)	2.80	2.81
N(2)···C(17)	2.73	2.73
N(4)···C(57)	2.79	2.78
N(5)···C(58)	2.79	2.80
N(2)···O(2)	2.59	2.59
N(4)···O(1)	2.59	2.59

(b) Intramolecular hydrogen bond data

Model A

N(1)···N(5)	2.71(1)	
N(1)···H(N1/N5)[a]	1.50(3)	Constrained to be equal
N(5)···H(N1/N5)	1.50(3)	Constrained to be equal
N(1)···H(N1/N5)···N(5)	130(5)	

Model B

N(1)···N(5)	2.72(1)	
N(1) - H(N1)[b]	1.08	Fixed bond lengths
N(5) - H(N5)[c]	1.08	Fixed bond lengths
H(N1)···N(5)	1.97	
H(N5)···N(1)	1.97	
H(N1)···H(N5)	1.00	
N(1) - H(N1)···N(5)	124	
N(5) - H(N5)···N(1)	124	

[a] Site occupancy factor (s.o.f.) = 1.00

[b] S.o.f. = 0.55(7)

[c] S.o.f. = 0.45(7)

arguments explain the orientation of the aryl ring attached to N(1); similar differences in exterior angles at the corresponding atoms are observed (Figures 6 and 7). That the two aryl groups are twisted in the same sense relative to the formazan ring is probably a result of molecular packing considerations in the crystal.

The nitro-group plane (Table 13, Plane 3) forms an angle of 23° with the formazan-ring plane (Plane 2), thereby decreasing non-bonded interactions between the oxygen atoms and N(2) and N(4) and between the lone-pair orbitals on both nitrogen and oxygen atoms: the O(1)···N(4) and O(2)···N(2) distances are both 2.59 Å and, *e.g.*, ω[O(1)-N(3)-C(3)-N(4)] is 22° (Tables 12 and 14). The formazan-chain-nitro linkage C(3)-N(3) (1.484 Å) compares to 1.475 Å in nitromethane[120] and is a single bond: electron delocalization in the formazan ring does not extend to the nitro group. However, the electron-withdrawing nitro-group will polarize the σ-electron density along the C(3)-N(3) bond thus reducing the repulsion between the σ electrons of this bond and those of the C(3)-N(2) and C(3)-N(4) bonds so allowing the N(2)-C(3)-N(4) bond angle to open from the expected sp^2 angle of 120° to 136°. By a similar argument the weakly electron-donating methyl groups on the aryl rings increase the σ-electron density along the (Ar)C-CH_3 bond and cause the corresponding interior angles to close to 116-119° (Figures 6 and 7); similar distortions have often been observed in substituted phenyl groups.[125] The N-O bond lengths of the nitro-group are nearly equivalent (Figures 6 and 7) and are normal for nitro compounds[119,120]

Molecular packing

The molecules are quite loosely packed in the crystal, and no intermolecular separations less than the sum of the van der Waals radii

according to Bondi [r(C) 1.77, r(H) 1.17, r(N) 1.60, and r(O) 1.50 Å][126] were found. The average volume occupied by a non-hydrogen atom (17.2 Å^3), however, is normal, as is the density of the crystals (1.31 g cm^{-3}) for this size of organic molecule. A projection of the molecular packing down the b-axis onto the (010) plane is shown in Figure 9. The moleculules are stacked in alternate directions along the b-axis; the crystal habit reflects this tendency in that preferential crystal growth is along b.

The imino hydrogen atom

A hydrogen bond is said to exist when a hydrogen atom is bonded to at least two atoms at the same time.[127,128] A hydrogen bond may thus be denoted A-H-B. However, in most hydrogen bond systems the bond A-H is much stronger than the bond H-B, thus allowing the interaction to be denoted A-H···B. A criterion often adopted for the existance of a hydrogen bond is that the distance d(H···B) shall be less than r(H) + r(B) - 0.2 Å, where r(H) and r(B) are the van der Waals radii for the H atom and the acceptor atom B, respectively.[127] However, this criterion was based on Pauling's value of 1.2 Å for r(H); recent neutron diffraction studies point to a value of 1.0 Å and the criterion now favoured discards the seemingly arbitrary correction of 0.2 Å to give d(H···B) < r(H) + r(B).[112] In most hydrogen bonds the atoms A and B are electronegative so as to ensure the presence of an acidic hydrogen on the donor atom A and a strong Lewis base B. The acceptor atom B nearly always possesses lone-pair electrons which are largely responsible for the formation of the hydrogen bond. Hydrogen bonding is favoured when the hydrogen bond angle A-H···B is near to 180°. However, Donohue[129] and Olovsson and Jönsson[112] have listed O-H···O, N-H···O, and N-H···N hydrogen bond data for many different compounds and conclude that a bent hydrogen bond is the rule

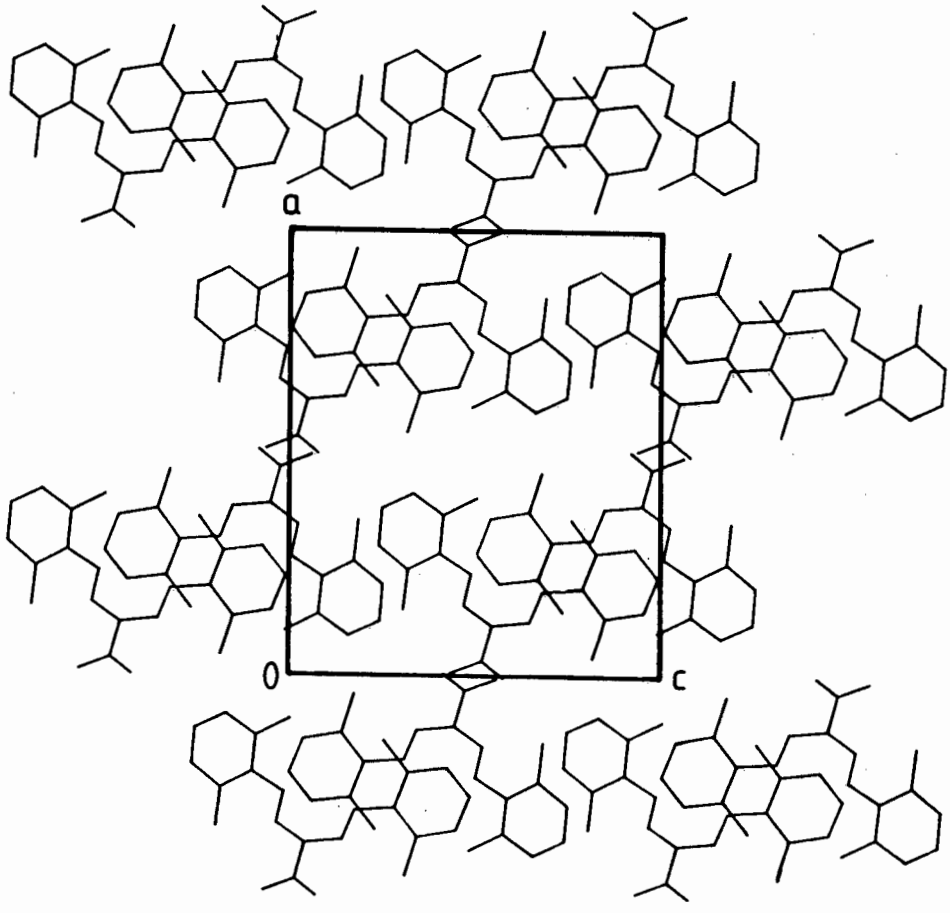


FIGURE 9 : Projection of the molecular packing of the nitroformazan (14) viewed down the *b*-axis onto the (010) plane.

rather than the exception; however, the angle is rarely less than 165° for a strong hydrogen bond. For weak bonds considerable deviations from 180° are often found;[130] stereochemical considerations affecting A and B, when they are parts of larger molecules, may preclude the pointing of A-H directly towards B.

Hydrogen bond data for Model A and Model B of the nitroformazan (14) are given in Table 14. The N···H distances for both models are significantly less than r(H) + r(N); however, the degree of uncertainty inherent in the *X*-ray diffraction method of locating hydrogen atoms requires that this criterion should also depend on the N···N distance. Clearly this requires that it be sterochemically reasonable for there to be a hydrogen atom in the region between the two nitrogen atoms. The N(1)···N(5) separation of 2.71 (Model A) or 2.72 Å (Model B) is somewhat shorter than the range quoted by Speakman[130] for an N-H···N hydrogen bond (2.8 - 3.2 Å). This does not mean that an exceptionally strong intramolecular hydrogen bond is present, however, for the stereochemistry of the sp^2-hybridized N(1) and N(5) does not allow linearity of the N···H···N or N-H···N angles. The former angle (Model A) is 130°, while the latter (Model B) is 124°, thus the hydrogen bond formed must to some extent be weakened. Hydrogen bonding is nevertheless favoured by the fact that in the configuration adopted (Model A or B) the lone pair of electrons on either terminal nitrogen atom points towards the hydrogen atom. Consideration of the angles around N(2) and N(4) (Figures 6 and 7) indicates a definite attraction of N(1) and N(5) towards each other, *i.e.*, towards the hydrogen bridge.

TABLE 15 : NOMENCLATURE FOR DIFFERENT H-BOND SITUATIONS[a]

H-bond situation		Crystallographic symmetry of the H-bond	
		(a) $\bar{1}$, 2, *m*, *etc*	(b) None
(I)	A···H···A	symmetric, centered	asymmetric, centered
(II)	A···(H,H)···A	symmetric, effectively centered	asymmetric, effectively centered
(III)	A··(H)··(H)··A	symmetric, disordered	asymmetric, disordered
(IV)	A — H···A	—	non-centered

[a]As proposed by Olovsson and Jönsson.[112]

The term 'symmetric hydrogen bond' has often been used to describe a situation in which the H-atom is located at the centre of the hydrogen bond, whether this is required by crystallographic symmetry or not. The term 'symmetric' is now used to describe the crystallographically symmetric case and the term 'centered' is used for all other cases.[112] The nomenclature outlined in Table 15 has recently been proposed by Olovsson and Jönsson.[112] In case (Ib) it is assumed that the H-atom deviates insignificantly from the centre of the A···A bond. In (II) the symbol (H,H) refers to a situation in which the H-atom is dynamically distributed between alternative positions very close to the centre of the A···A bond. In (III) these alternative positions are further apart and the potential barrier may be somewhat higher, with a possibility for either static or dynamic disorder. Naturally no clear dividing lines exist between the different situations indicated, but our Model A for the nitroformazan (14) clearly corresponds to type (Ib), whereas our Model B

corresponds to type (IIIb).

The main factor favouring Model A is the observation of a centered peak of electron density in the difference map (Figure 4), while the main factor favouring Model B is the very much lower temperature factor for the two half-hydrogens. Also favouring Model B are the realistic N-H bond lengths. On the other hand the Model A parameters generally have fractionally lower e.s.d.'s than the Model B parameters (Tables 7, 9, 10 and 11), and the final R value is lower, although this last factor has been shown to be insignificant. It must be emphasized that both models were subjected to exactly the same number of least-squares cycles in the final refinement, starting from exactly the same set of partly-refined parameters: only the imino hydrogen parameters were different.

One possible interpretation of these results which applies particularly to Model B, both with regard to the low temperature factors for the two half-hydrogens of the imino proton and the delocalized character of the formazan chain, might be that the crystal is statically disordered, containing a random mixture of two individual tautomers corresponding to [(2a); $R^1 = R^2$ = 2,6-dimethylphenyl, $R^3 = NO_2$] and the equivalent form with the imino hydrogen and both the double bonds moved (2b). These would properly be called tautomers if there were a significant barrier to their interconversion; the evidence presented in the next Section of this Chapter (*q.v.*) is against this suggestion. However, even if in fact these two distinct species *might* exist, the evidence is against their co-existing in this crystal. The anisotropic thermal motion parameters (Table 9) have normal values and give no evidence of the high apparent tangential motion of the atoms in the formazan ring which

such a disorder would simulate. While it is not unequivocally established that there are two equivalent proton positions rather than a single average one, the results do clearly suggest that the barrier in the potential function for movement of this proton must be relatively low, and the function itself nearly symmetrical. In any case, the distinction between a symmetric double-minimum potential and a single-minimum potential is, in practice, often of a highly tenuous nature. The two minima in the former case can be close together, while in the latter case, the breadth and shallowness of the potential can mean that the vibrational amplitude of the proton is greater than for other types of potential curves.[131] This may be what is observed in Model A, where U[H(N1/N5)] is 0.25 Å^2 compared with 0.11 Å^2 for both half-hydrogens of Model B; thus the higher temperature factor for the imino hydrogen in Model A may actually be taken to support this model. In either case the position of the proton may be smeared (although see Figure 4), and Lundgren and Olovsson point out that 'it is practically impossible to differentiate, on the basis of diffraction data alone, between two overlapping disordered hydrogen peaks and a truly single central peak'.[131] To reduce the effect of thermal motion, this type of investigation should be carried out at as low a temperature as possible.

It has been suggested by Rundle[132] that the isotope effect, *i.e.*, the change in the length of the short hydrogen bond on substituting deuterium for hydrogen, can be used to differentiate between single- and double-minimum H-atom potentials; an *X*-ray structure determination of the deuterated analogue of the nitroformazan (14) would therefore be interesting. The deuterated analogue was synthesized in this work and shown by comparison with the spectroscopic properties of its parent compound very

probably to have the same structure (see following Section).

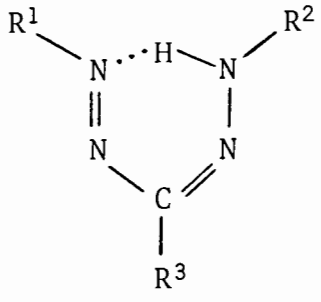
Short hydrogen bonds with apparently disordered hydrogen atoms have been reported in a number of structures recently, *e.g.*, cytosine-5-acetic acid,[135] β-5-n-propoxy-*o*-quinone-2-oxime,[134] and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (20),[114] while proton tunnelling in N-H···N bonds has been discussed in connection with genetic mutations involving the guanine-cytosine base pair of deoxyribonucleic acid.[135] A precise *X*-ray study of porphine shows a half-hydrogen atom associated with each nitrogen atom and apparent equivalence of chemical bonds which would be distinct in individual tautomers.[136] In the structure of the hydrochloride of 'diformazyl' (19),[100] on the other hand, the imino proton is found on N(1) and N(5) with site occupancy factors of 0.35 and 0.65, respectively, and the formal single and double bonds in the N-N-C-N-N chain are clearly distinguishable and correspond to the fraction of hydrogen atom on each of the terminal nitrogens.

Nature of the formazan ring

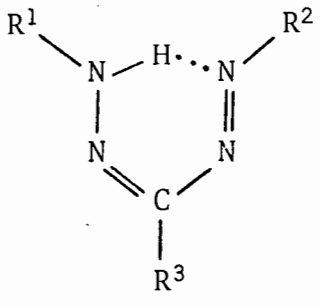
The formal single and double bonds in the structure of the nitroformazan (14) are not distinguishable and the s.o.f.'s of 0.55(7) and 0.45(7) for Model B's H(N1) and H(N5), respectively, do not correspond to the allocation of formal single and double bonds based upon the small difference in C-N lengths in the formazan chain. The e.s.d.'s of the s.o.f.'s, however, are quite large and the imino proton may be considered equally shared between N(1) and N(5) (in both models), especially since the two N-N distances in the molecule (for both models) are identical (within the e.s.d.'s). It is interesting that in the *X*-ray structure of the bis-complex of 3-methyl-1(or 5)-phenyl-5(or 1)-*p*-tolylformazan with Ni(II) the metal atom occupies the position of the centered imino proton

of our Model A for the nitroformazan (14); the positions 1 and 5 appear from the calculated electron density to be occupied by phenyl and tolyl groups in the proportion of 0.45 : 0.55, and the presence of disorder has been suggested.[97] That this ratio is the same as that observed here for the proportion of imino hydrogen found on positions 1 and 5 in Model B seems fortuitous. In this metal complex the N-N bond lengths are virtually identical [1.318(9) and 1.313(8) Å] while there may be a small difference in C-N lengths [1.341(10) and 1.330(10) Å]

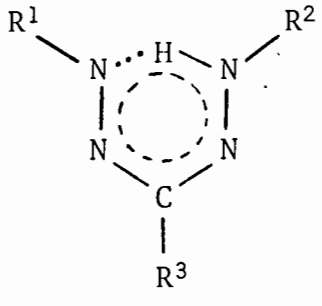
The difference (0.024 Å) in the formazan ring C-N lengths in the nitroformazan (14), however, is four times the e.s.d.'s and appears to be real. No explanation has been found for this disparity, which may be a result of molecular packing considerations in the crystal, although no close contacts were found. The disparity in the C-N lengths does correspond with Schiele's model for closed-chain formazans mentioned earlier, *viz* a hybrid involving structures (2a) and (2k), where a slight asymmetry of electron delocalization was predicted.[80-83] It seems more likely,



(2a)

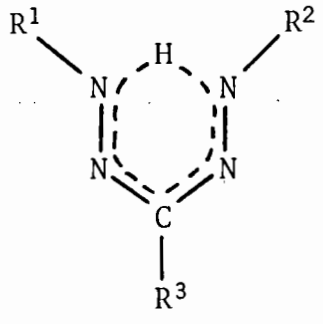


(2b)



(2k)

however, that the very small disparity should be considered real but not particularly meaningful, and that the simplest picture to consider is the superimposition of two equivalent resonance forms, corresponding to [(2a); R^1 = R^2 = 2,6-dimethylphenyl, R^3 = NO_2] and the equivalent form with the double bonds all shifted to the neighbouring position and the bond from N to H transferred to the other nitrogen atom (2b). This view would lead one to expect the formazan ring C-N and N-N bonds to correspond to the aromatic distance, which indeed they do. This then constitutes a mesomeric structure, best represented by structure (2c),

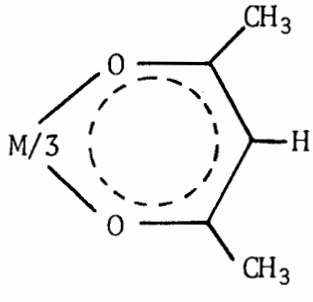


(2c)

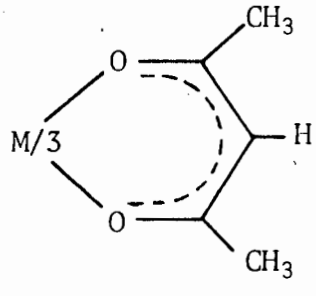
derived as a resonance hybrid (in valence-bond terminology) of the two limiting forms (2a) and (2b). In molecular-orbital terminology the system would simply be described as 'electron-delocalized'. In this description the adoption of either Model A or Model B is not important and the imino proton need simply be considered as being somewhere between N(1) and N(5) with a relatively low barrier in the potential function, which itself may be nearly symmetrical.

This kind of structure for the *syn*,s-*cis* formazans (2c) has on occasion been described as 'quasi-aromatic'.[59,82,95] This term has been

applied to the diamagnetic metal acetylacetonates which have been found to undergo replacement reactions of the hydrogen atoms bonded to sp^2-hybridized carbon atoms.[137,138] These reactions are effected by reagents and under conditions typical of substitution reactions of benzenoid compounds and the chelates have, therefore, been termed quasi-aromatic.[138] It has been argued[137] that each chelate ring has a cyclic π-orbital, formed by overlap of vacant *d*-orbitals of the central metal atom with the six π-electron orbital of the ligand, although contrary views have also been expressed.[139] If the π-orbital is cyclic (21a) the compounds can properly be called aromatic. If, however, it is acyclic (21b) they are not aromatic and in view of their chemical character they are best described as quasi-aromatic.[140] The correct π-electron structure of acetylacetonates is, however, still in doubt.

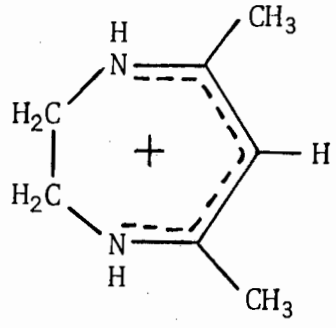


(21a)



(21b)

That such an acyclic π-electron system can have chemical properties similar to those of aromatic compounds has been shown independently by the chemisty of the isoelectronic 5,7-dimethyl-2,3-dihydro-1,4-diazepinium system (22), which forms a very stable, singly protonated

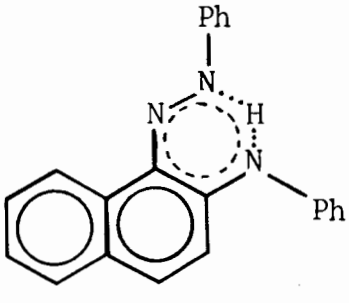


(22)

cation.[142] The hydrogen atom at the 6-position readily undergoes substitution reactions[143] and the mechanisms of bromination and of iodination appear to parallel those of the corresponding reactions of aromatic compounds such as phenol and aniline.[144] The π-electron system is undoubtedly acyclic since part of the ring is made up of sp^3- hybridized atoms and is best described as quasi-aromatic. In 1964 Lloyd and Marshall[140] proposed a definition based on their studies of these systems: 'Molecules should be called quasi-aromatic only if they contain an acyclic, conjugated π-electron system and show chemical properties typical of aromatic compounds, especially reaction by substitution with retention of type. A significant mesomeric stability is implied'. (The term 'pseudo-aromatic' has an opposite meaning,[140] describing molecules with cyclic, formally conjugated systems of double bonds, but without mesomeric stability and without chemical character of an aromatic type.)

The term 'quasi-aromatic' is inappropriate as a description of the nitroformazan (14) because while the first part of Lloyd and Marshall's definition is satisfied (acyclic, conjugated π-electron system), the reactions of the formazans in general are not typically aromatic and reactions by substitution at the 3-carbon with retention of type are virtually unknown.[145]

This definition of quasi-aromaticity resulted in several systems bearing resemblance to the formazan ring and previously described as quasi-aromatic being re-styled as 'non-classical aromatic'.[146] Among these were the 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (20) mentioned above,[147] 1-phenylazo-*N*-phenyl-2-naphthylamine (23),[148] 2-benzylamino-4-benzylimino-2-pentene (24),[146] and the sugar osazones (25).[149,150] These 'non-classical aromatic' systems were said to involve π-electronic interaction or



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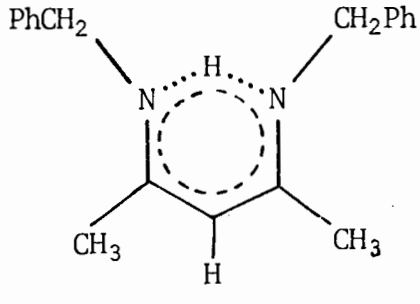

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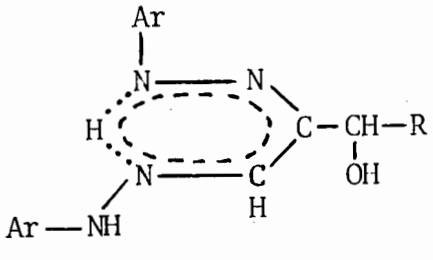
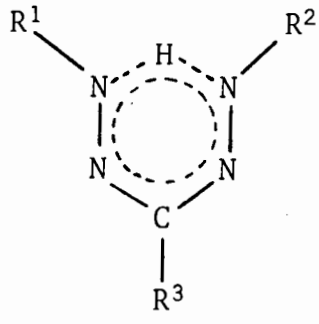


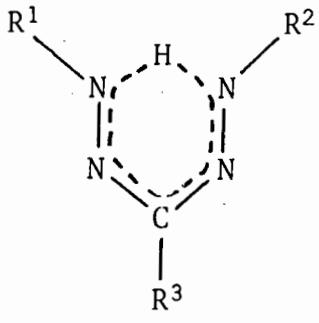
(25)

electron delocalization through the hydrogen bond.[146] Some of the evidence included molecular-orbital calculations, which when performed on (23) to determine the total π-electron energies, indicated that a π-electron interaction through the hydrogen bond probably exists, based on the total π-electron energies;[148] *X*-ray data showed that the 6-membered chelate ring in the *p*-bromophenylosazone of D-xylose [(25); Ar = *p*-bromophenylosazone, R = $CHOH.CH_2OH$] is essentially coplanar with the aryl rings and has bond angles around 120°, but the hydrogen atoms were not located;[151,152] n.m.r. and i.r. spectroscopic measurements were used to ascribe aromatic character to (20)[147] and (24).[146] Each of these systems obeys Hückel's rule[153] and possesses $(4n + 2)$ π-electrons [n = 1 : (23), (24), (25); n = 2 : (20)]. However, by comparison of the u.v. and n.m.r. spectroscopic data of (23) with those of the corresponding cyclically and acyclically conjugated model compounds, Daltrozzo and Feldmann[154] have shown that the electronic structure of these 'non-classical aromatic' hydrogen chelates is not cyclically conjugated. Thus although the formazans also possess a six π-electron system [involving two formal double bonds (:C=N- and -N=N-) and the lone pair of electrons from one of the nitrogens] the likelihood of π-electronic interaction through the hydrogen bond appears remote, especially considering the relatively facile temporal isomerization of most red formazans to a yellow form upon dissolving in organic solvents; π-electronic interaction through the hydrogen bond would make isomerization unlikely considering the consequent loss of resonance stabilization energy, and it is difficult to envisage which orbitals on the hydrogen atom would be used to conduct any 'ring current' in a cyclically conjugated 'non-classical aromatic'

formazan represented by (27). In addition, the imino proton in the



(27)



(2c)

penultimate electron density difference map (Figure 4) of the nitroformazan (14) appeared as a sharp centered peak rather than as the broad smear of electron density expected in a cyclically conjugated structure. Thus the structure of the nitroformazan (14) in the solid state seems best represented by the mesomeric strucutre [(2c); $R^1 = R^2 = 2,6$-dimethylphenyl, $R^3 = NO_2$], as originally contemplated by Kuhn and Jerchel[24] and Hunter and Roberts,[26] while the spectroscopic results reported in the following Section extend the results of this *X*-ray crystal structure determination to the nitroformazans (9) - (17) (Table 2) both as solids and in solution.

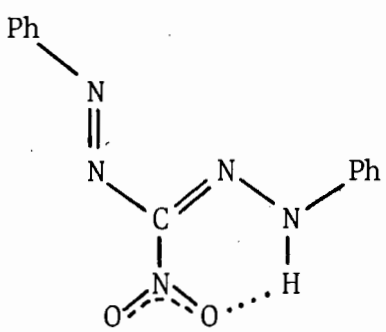
It may finally be noted that the curiously small yields of (14) and (15) obtained repeatedly in their synthesis, and discussed earlier in this Chapter, cannot be ascribed to any special feature of the molecular structure as exemplified by (14).

3. Spectroscopic studies

Having established the structure of 3-nitro-1,5-di(2,6-dimethylphenyl)-formazan (14) by *X*-ray crystallography, attention was turned to the complete series of nitroformazans with variously substituted aryl groups [(9) - (17)]. The diffuse reflectance spectra of the complete series (9) - (17) taken as nujol mulls on filter paper showed in each case a broad $\lambda_{max.}$ centered at 460 nm. Thus the conjugated system giving rise to the chromophore appears to be unchanged through the series, since an isomer different from the *syn*,s-*cis* structure found for (14) would absorb at a somewhat different wavelength. For example, 1,5-diphenylformazan, which forms yellow crystals known[91] to comprise molecules in the open *anti*,s-*trans* configuration [(2f); $R^1 = R^2 = Ph$, $R^3 = H$], shows a broad maximum at 400 nm in the diffuse reflectance spectrum.

No N-H stretching frequency was observed in the i.r. spectra of any of the nitroformazans (9) - (17) as KBr pressed disks, the ν(N-H) vibration possibly being masked by ν(C-H) vibrations. Such a low frequency for ν(N-H) would indicate a strong hydrogen bond or certainly a hydrogen atom in an unusual environment, as expected from the *X*-ray crystal structure of (14). The lack of observed ν(N-H) in *syn*,s-*cis* formazans has been noted by previous workers.[32,58] A temperature sensitive band at *ca.* 3030 cm^{-1} has been assigned to ν(N-H) in these compounds[83] but the present work has shown that this band does not move on deuteration. In addition, no new band could be found in the i.r. spectrum of the deuterated analogue of (14) which might be assigned to ν(N-D). This deuterated analogue of (14) gave a diffuse reflectance spectrum identical with that of its parent compound. In view of the similarity of the diffuse reflectance and i.r. spectra, it seems safe to say that the complete series of red nitroformazans (9) - (17) and deuterated analogues has the same mesomeric *syn*,s-*cis* structure as found for (14) by *X*-ray crystallography.

The similarity of the visible absorption spectra (Table 16) of the nitroformazans (9) - (17) in chloroform solution indicates that the series is isostructural in solution as well as in the solid state. The slightly higher energy absorptions of (14) and (15) are probably a result of steric effects due to the methyl groups in the *ortho*-positions giving rise to a slightly shorter conjugated system as the aryl groups are twisted away from the plane of the formazan ring [*cf.* the crystal structure of (14)]. The i.r. spectra of CCl_4 solutions in the ν(N-H) region are identical with the solid state spectra, and again no trace of ν(N-H) or ν(N-D) was found. The suggestion by Gill, Irving, and Prescott[58] in their study of acid strengths of various substituted formazans in ethanolic solution, that the nitroformazan (9) is stabilized in a molecular non-titratable form by intramolecular hydrogen bonding with the nitro-group in an *anti*,s-*cis* configuration [as (9a)] is now considered unlikely in view of the similarity



(9a)

TABLE 16 : VISIBLE ABSORPTION[a] AND ^{1}H N.M.R. SPECTROSCOPIC DATA FOR THE 3-NITRO-1,5-DIARYLFORMAZANS (9) - (17)

No.	Aryl group	λ/nm	ε/m^2 mol^{-1}	δ(N*H*)[c]	δ(C*H*, C*H*$_2$, or C*H*$_3$)	δ(Ar*H*)
(9)	phenyl	452	2358	15.28	-	7.60 (m, 10H)
(10)	*p*-tolyl	463	2555	15.34	2.40 (s, 6H)	7.29 (d, *J* = 8 Hz, 4H) 7.63 (d, *J* = 8 Hz, 4H)
(11)	*m*-tolyl	456	2375	15.29	2.46 (s, 6H)	7.40 (m, 8H)
(12)	*o*-tolyl	452	2226	15.24	2.55 (s, 6H)	7.50 (m, 8H)
(13)	3,5-dimethylphenyl	460	2365	15.25	2.42 (s, 12H)	7.04 (s, 4H) 7.34 (s, 2H)
(14)	2,6-dimethylphenyl	441	1929	14.50	2.50 (s, 12H)	7.20 (s, 6H)
(15)	2,4,6-trimethylphenyl	443	2019	14.43	2.34 (s, 6H) 2.46 (s, 12H)	6.99 (s, 4H)
(16)	*p*-isopropylphenyl	464	2476	15.31	1.30 (d, *J* = 7 Hz, 12H) 2.97 (h, *J* = 7 Hz, 2H)	7.34 (d, *J* = 8 Hz, 4H) 7.66 (d, *J* = 8 Hz, 4H)
(17)	*p*-n-butylphenyl	469	2617	15.39	0.94 (t, *J* = 7 Hz, 6H) 1.45 (m, 8H) 2.68 (t, *J* = 7 Hz, 4H)	7.30 (d, *J* = 8 Hz, 4H) 7.64 (d, *J* = 8 Hz, 4H)

[a] Measured in chloroform.

[b] 100 MHz spectra in $CDCl_3$ at ambient temperature. Chemical shifts (δ,ppm) are relative to $(CH_3)_4Si$. Abbreviations used: s, singlet; d, doublet; t, triplet; h, heptet; m, multiplet.

[c] All singlets integrating for 1H and slowly disappearing on addition of D_2O.

of the wavelengths of the maxima in the diffuse reflectance and absorption spectra. In addition, the nitro-group stretching frequencies at 1540 and 1355 cm^{-1} (KBr pressed disk) in (9) do not shift in solution spectra (CCl_4), indicating no new interaction of the nitro-group upon dissolution. In their study, Gill *et al.*[58] showed that the nitroformazan (9), as with all the formazans stable only as their red isomers, was too weakly acidic for titration even with very strong sodium ethoxide solutions. It is thus clear that the closed ring *syn*, s-*cis* formazans possess little tendency to protonate even very basic species, and this fact might be explained by the unusual hydrogen bonding situation of the imino proton in this configuration.

The ^1H n.m.r. spectra of the nitroformazans (9) - (17) (Table 16) indicate equivalence of the two aryl rings and their substituents with respect to the n.m.r. time-scale. Non-equivalence would be expected in configurations other than the closed ring *syn*,s-*cis* structure due to the magnetic anisotropy effect of the azo-group, especially in compounds (12), (14), and (15), where there are methyl groups in *ortho*-positions. That the singlets (Table 16) given by these methyl groups are quite unperturbed even at -40°C indicates that either the molecules exist in a very rapid tautomeric equilibrium [as (2a) $\rightleftharpoons$ (2b)] or they exist in the single mesomeric structure (2c) as found in the solid state by *X*-ray crystallography; otherwise the effect of isolated single :N-N: and double -N=N- bonds on the *ortho*-methyl groups would differ and two methyl peaks would be observed. Except for a small change in chemical shift values, the aromatic and aliphatic ^1H resonances in the nitroformazans (9) - (17) are identical to those of the corresponding precursive anilines, where,

of course, only one form of the molecule is possible. The mesomeric structure (2c) is favoured by the sharp very low field imino proton resonance at *ca.* δ 15.3 (Table 16) which disappears only slowly on washing with D_2O. The chemical shifts of these imino protons are in full agreement with extensive deshielding resulting from a single mesomeric structure, while the slightly smaller shifts (*ca.* δ 14.5) found in (14) and (15), where there are methyl groups in both *ortho*-positions on the aryl rings, are probably the result of a slightly shorter conjugated system formed as steric interaction twists the aryl groups away from the plane of the formazan ring. In contrast, it was found that 3-chloro-1,5-diphenylformazan, which is a yellow solid with a $\lambda_{max.}$ in chloroform at 410 nm and is probably in the open chain *anti*,s-*trans* configuration, gave a N*H* resonance at δ 8.72 in $CDCl_3$ and an obvious ν(N-H) at 3258 cm^{-1} in CCl_4.

If N(1) and N(5) in the nitroformazan (9) are replaced by 96 atom-% ^{15}N (spin quantum number = ½) the N*H* line at δ 15.28 becomes a triplet (1:2:1) centered at δ 15.28 with an apparent coupling constant of 46.0 Hz for both ^{15}N atoms. This value falls outside the usual range of ^{15}N-H coupling values [*ca.* 90 Hz for structurally related compounds such as the sugar osazones (25)[155]] and could indicate an averaging[156] of the ^{15}N-H coupling over two chemically equivalent nitrogen sites consistent with the rapid tautomeric equilibrium (2a) $\rightleftharpoons$ (2b). However, the spin coupling constant is known to vary with N-H bond length (bond order) and hybridization of the nitrogen,[157,158] and it is not difficult to envisage the normal ^{15}N-H coupling constant being halved in the mesomeric structure (2c), where the hydrogen atom is formally situated at an equal distance from N(1) and N(5) with a consequent increase in N-H distance and decrease in ^{15}N-H coupling. Neither the chemical shift nor

$^{1}J(^{15}N\text{-}H)$ changed in the spectrum run at -40°C, which indicates that if a rapid intramolecular proton exchange does occur, it has a very small energy of activation indeed. These results concur with those of previous workers who have observed ^{15}N-H coupling constants in formazans;[75-78] these workers, however, have always interpreted their results in terms of a rapid tautomeric equilibrium between forms (2a) and (2b), but their results do not exclude the possibility of a mesomeric structure [as (2c)] which certainly exists in the solid state.

The direct observation of the ^{15}N nucleus by n.m.r. at natural abundance level (0.36%) has been made possible in the past 10 years by advances in technique, specifically by the innovation of the pulse-Fourier transform method with ^{1}H noise decoupling. The range of nitrogen chemical shifts in organic compounds is about 800 ppm, and in tautomeric pairs of molecules the corresponding relative shifts in ^{15}N n.m.r. are large. The experimental aspects and the large literature on ^{15}N chemical shifts and coupling constants have been reviewed depth.[159] The sensitivity of ^{15}N in an n.m.r. experiment at constant field compared with ^{13}C (both isotopes at natural abundance) is about 1 : 30. Thus, to obtain comparable signal-to-noise ratios from experiments using signal averaging on the two species at similar total nitrogen and carbon concentrations would take about 900 times longer for ^{15}N than for ^{13}C, which is already a difficult nucleus. Isotopic enrichment provides a means of increasing the sensitivity.

The ^{15}N n.m.r. spectrum in $CDCl_3$ of the nitroformazan (9) labelled at N(1) and N(5) with 96 atom-% ^{15}N (Figure 10) shows a single peak when observed with broad-band proton decoupling both at ambient temperature (*ca.* 31°C) and at -40°C; this indicates that, on the n.m.r. time-scale, N(1) and N(5) are equivalent. The proton-coupled spectrum (Figure 10, inset) exhibits a doublet with $^{1}J(^{15}N\text{-}H)$ = 46 Hz, the same value as observed in the proton spectrum of the ^{15}N-labelled compound. The two equivalent nitrogens give rise to a single line which is split into a doublet by the one imino proton. This result as well may be interpreted either in terms of an extremely rapid tautomeric equilibrium (2a) $\rightleftharpoons$ (2b) or a single mesomeric structure [as (2c)]. The chemical shift of the ^{15}N resonance in the labelled nitroformazan (9) is found 223 ppm downfield from external $[^{15}N(CH_3)_4]^+$. This corresponds to an intermediate shift between that of azobenzene, PhN=NPh (462 ppm), and hydrazobenzene, PhNH-NHPh (51ppm).[160] Again it is not possible to say whether the observed peak is a time-average of two different nitrogen resonances corresponding to (2a) $\rightleftharpoons$ (2b), or whether the intermediate shift results from electron delocalization as in the single mesomeric structure (2c). A 'non-classical aromatic' structure (2*l*) seems excluded by comparison with the ^{15}N shift of 337 ppm for the aromatic 1,2,4,5-tetrazine (27),[160] and the observed shift is more comparable with the average resonance signal (200 ppm) given by 1,2,4-triazole (28);[160] the signal in the nitroformazan (9), however, is further deshielded due to the increased screening resulting from greater double-bond character of the N-N bond in (9). The unlabelled N(2) and N(4) nitrogens were not observed.

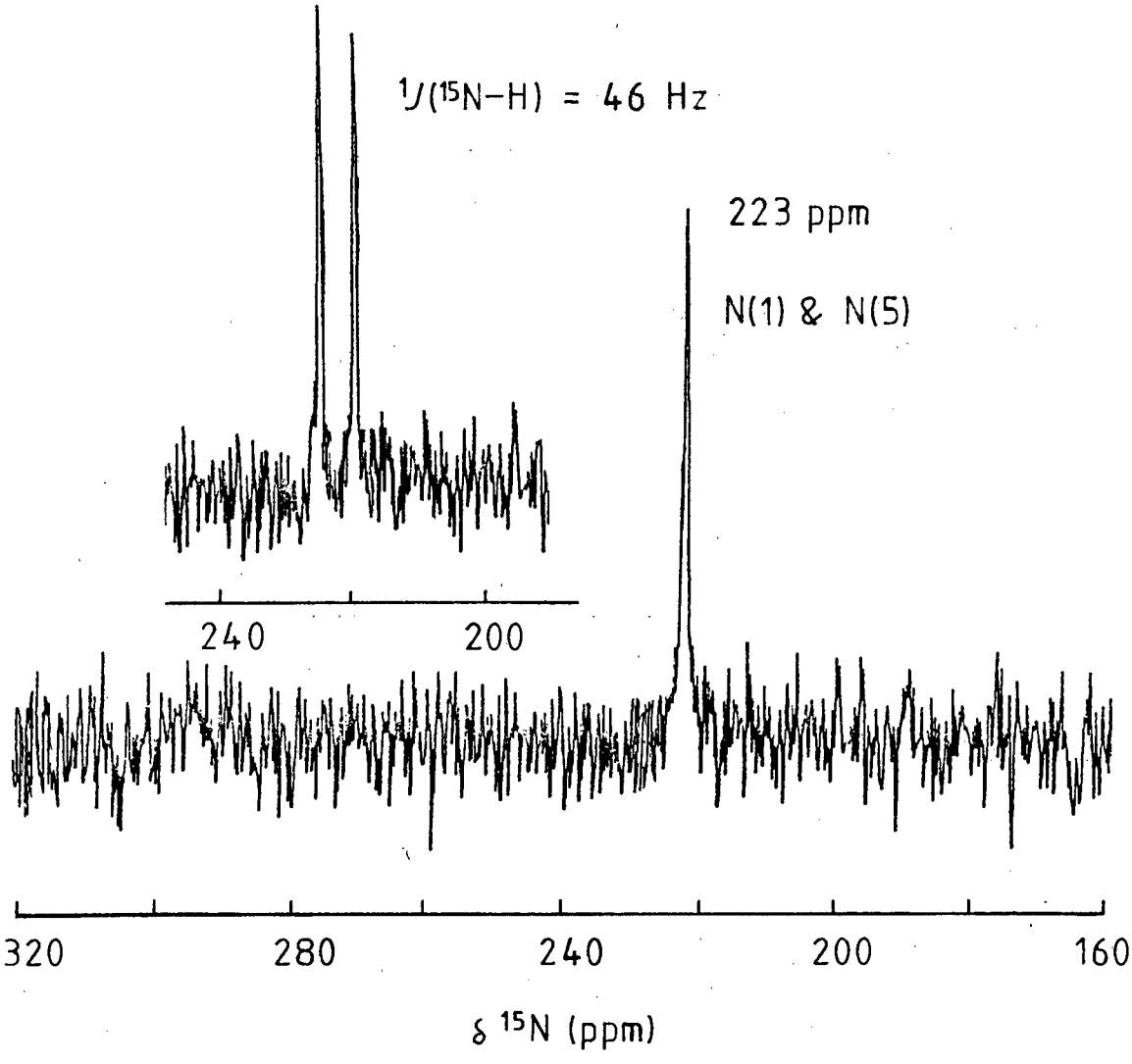
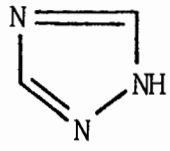


FIGURE 10 : Proton-decoupled ^{15}N n.m.r. spectrum of the nitroformazan (9) labelled at N(1) and N(5) with 96 atom-% ^{15}N. Chemical shifts are down field from external $[^{15}N(CH_3)_3]^+$. Inset: corresponding proton-coupled spectrum.

(27)



(28)

The ^{13}C n.m.r. spectrum in $CDCl_3$ of the nitroformazan (9) labelled at C(3) with 91 atom-% ^{13}C (Figure 11) gives a single peak (whether observed with or without proton-decoupling) at 171.0 ppm downfield from tetramethylsilane. This compares well with the aromatic carbon resonance in 1,2,4,5-tetrazine (27) (161.9 ppm),[161] but if the strongly deshielding effect of the nitro-group is taken into account (usually shifting the ^{13}C resonance downfield by *ca.* 20 ppm relative to the unsubstituted carbon[162]),the ^{13}C signal in the nitroformazan (9) corresponds more to the kind of carbon atom in the 3-position of 1,2,4-triazole (28) (148.1 ppm).[161] The ^{13}C spectrum provides no more information than confirming the conjugated nature of the N-N-C-N-N formazan chain. The unlabelled carbon atoms were not observed because the small amount of material available and its relative insolubility necessitated working with solutions not concentrated enough to overcome the low natural abundance of ^{13}C (1.1%).

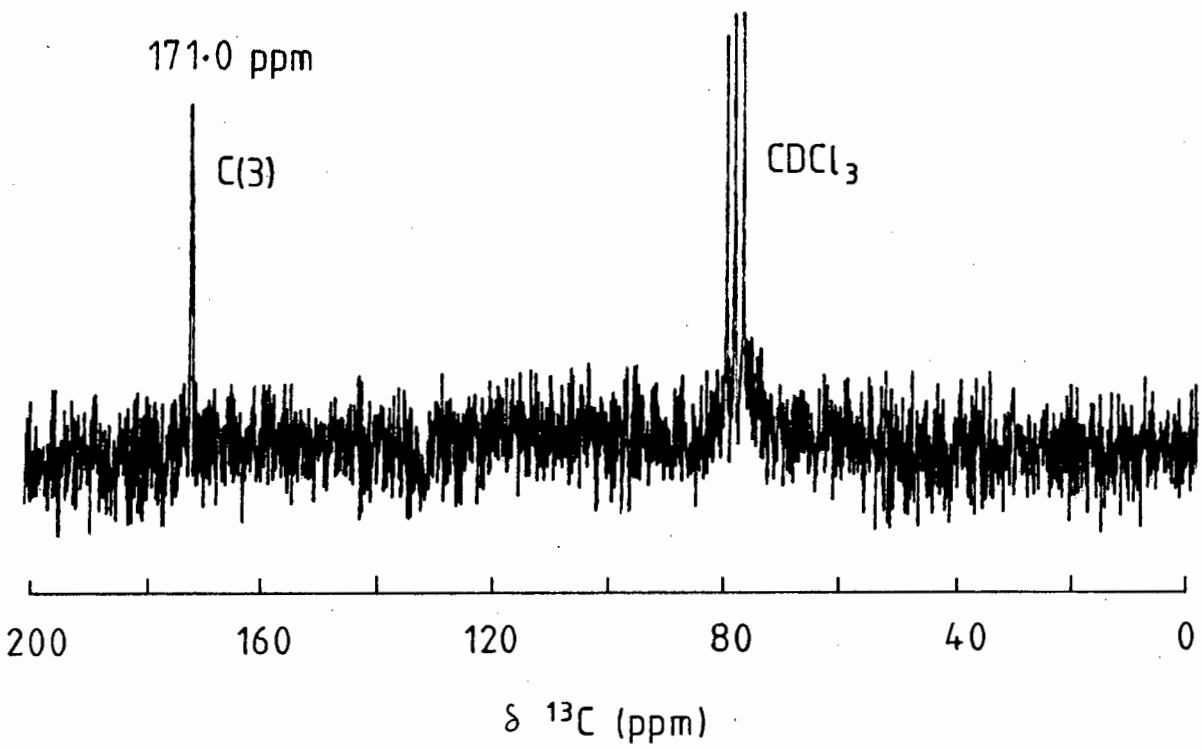


FIGURE 11 : Proton-decoupled ^{13}C n.m.r. spectrum of the nitroformazan (9) labelled at C(3) with 91 atom-% ^{13}C. Chemical shifts are downfield from external $Si(CH_3)_4$.

The results of the spectroscopic measurements carried out on chloroform solutions of the symmetrical [(2); $R^1 = R^2 =$ Ar] nitroformazans (9) - (17), their deuterated analogues, and the ^{15}N- and ^{13}C-enriched analogues of (9), neither confirm nor deny the possibility of a single mesomeric structure [as(2c)] for these compounds in chloroform solution. This structure is certainly supported by the *X*-ray crystal structure of (14) and even if, upon dissolution in chloroform, the extremely rapid tautomeric equilibrium (2a) $\rightleftharpoons$ (2b) does exist, the special kind of tautomerism involved in the case of the symmetrical closed-ring *syn*,s-*cis* formazans, which amounts simply to a movement of electrons and slight displacement of the imino proton, rather than an actual migration of a hydrogen atom such as occurs in keto-enol tautomeric systems like acetylacetone, must have an extremely small energy of activation. From this point of view, such an extremely rapid and facile proton exchange may (in the limit as the rate of exchange becomes very large) produce an effect equivalent to, and indistinguishable from, a single electron-delocalized mesomeric structure. However, this then becomes a problem more suitable for the theoretician, if not the philosopher. These conclusions apply only to the symmetrical nitroformazans and it would be interesting to observe the effect of differing aryl groups at the terminal nitrogens [(2); $R^1 \neq R^2$] on the molecular structure as revealed by crystallography and spectroscopy.

4. Experimental

General and spectroscopic

All the solvents used for spectroscopic work were of spectroscopic grade, *e.g.* Uvasol grade from Merck, Darmstadt, and stored over molecular sieve. Standard solutions of the nitroformazans (9) - (17) were prepared as required by weighing out suitable quantities on a micro-balance and dissolving in the spectroscopic solvent (100 ml volumetric flasks). Appropriate portions of these stock solutions were taken and diluted as required to prepare the working solutions.

Electronic spectra were recorded on a Varian Superscan 3 u.v.-visible spectrophotometer using 1.00 cm matching quartz cells. The cells were kept at 20° by water circulated from a thermostatically regulated bath. Diffuse reflectance spectra were taken as nujal mulls on filter paper using a Beckman DK-2A ratio recording spectrophotometer in the reflectance mode.

Infrared spectra were measured from 4000 - 600 cm^{-1} as KBr pressed disks (3 mg sample in 300 mg dried KBr) on a Perkin Elmer 180 spectrophotometer. Matched Beckman NaCl solution cells with a 0.5 mm path length were used to obtain spectra of the nitroformazans in carbon tetrachloride solution.

Proton n.m.r. spectra were obtained at 100 MHz on a Varian XL-100 continuous wave spectrometer at ambient temperature (*ca.* 31°C) and at -40°C. Deuterochloroform was n.m.r. grade from Merck, D_2O was 99.8 atom-% isotopic purity from Goss, London. Chemical shifts are quoted relative to tetramethylsilane (TMS) and are considered accurate to

±0.05 ppm, while coupling constants are estimated to ±0.5 Hz.

^{13}C n.m.r. spectra were obtained on a Bruker WH-90DS pulse Fourier transform spectrometer operating at 22.63 MHz and using 10 mm diameter n.m.r. tubes. The probe temperature was *ca.* 40°C with broad-band ^{1}H decoupling at 1.0 W power. Typically a 30° pulse with a 1 second delay was used with an acquisition time of 682 milliseconds. Suitable spectra were obtained from solutions of concentration *ca.* 0.1 *M* requiring about 9000 transients. Shifts were taken relative to the central line of the $CDCl_3$ ^{13}C signal, which resonates at 76.9 ppm relative to TMS,[161] and are accurate to an estimated 0.1 ppm.

^{15}N n.m.r. spectra were obtained on the Bruker instrument operating at 9.12 MHz. Spectra were recorded with noise-modulated ^{1}H decoupling (3.3 kHz), and some measurements were taken in the gated proton irradiation mode allowing the observation of proton coupled but intensity enhanced spectra by the nuclear Overhauser effect (NOE).[163] Due to the expected large spin-lattice relaxation times (T_1) associated with ^{15}N nuclei,[164] a delay of 5 seconds was used between 30° pulses (341 millisecond acquisition time), and *ca.*4000 transients were collected overnight. Sample concentration was *ca.* 0.1 *M* and 10 mm n.m.r. tubes were used. The use of shiftless relaxation agents such as chromium(III) acetylacetonate[163] was prohibited by the need to recover the sample for further use in the synthesis of ^{15}N-labelled dithizone. Shifts are reported relative to external tetramethylammonium ion on the frequency scale of nitrogen chemical shifts[160] and are accurate to 1 ppm, while coupling constants are estimated to ±1 Hz. The Bruker variable temperature control provided sample temperatures down to -40°C.

Preparations

All reagents were analytically pure and generally supplied by Merck, Darmstadt. Substituted anilines were provided by the Aldrich Chemical Company and were distilled over zinc dust before use. Except for spectroscopic work, or unless otherwise stated, solvents used were laboratory reagent grade. Chloroform for extraction purposes was obtained chloride-free by shaking with glass-distilled water and then drying with sodium sulphate. Glass-distilled water was used throughout. All preparative chromatographic work was carried out with columns (35 x 2.5 cm) prepared using a slurry in benzene of aluminium oxide (alumina) standardised for chromatographic adsorption analysis according to Brockmann (Merck, activity grade II-III). All melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected. Microanalyses for C, H, and N were performed on a Heraeus Universal Combustion Analyser, Model CHN-Micro, by Mr. W.R.T. Hemsted of the Department of Organic Chemistry, University of Cape Town.

3-Nitro-1,5-diphenylformazan (9)

Sodium hydroxide pellets (4.0 g; 0.10 mol) were dissolved in distilled water (15 cm^3) and cooled in an ice bath to 0°C. A solution of nitromethane (6.4 g; 0.10 mol) in ethanol (35 cm^3) was added slowly with constant mechanical stirring and keeping the temperature below 0°C. About 500 g of ice water and crushed ice was added to dissolve the white precipitate and the solution was kept at 0°C until used. Freshly distilled aniline (18.6 g; 0.20 mol) was added to a mixture of concentrated hydrochloric acid (60 cm^3) and distilled water (100 cm^3) in a 2 litre beaker. The resultant clear solution was cooled to 0°C in an ice-salt bath and diazotized by adding dropwise and with mechanical stirring a solution of

sodium nitrite (16.6 g ; 0.24 mol) in distilled water (30 cm^3). Filtration of the clear yellow solution was not necessary and sodium acetate (41 g; 0.5 mol) dissolved in distilled water (120 cm^3) was added dropwise, keeping the temperature at 0°C, to buffer the solution at about pH 4.5. The alkaline nitromethane solution was placed in a separatory funnel containing crushed ice and dropped slowly, with vigorous mechanical stirring, into the diazotized solution. The required nitroformazan (9) separated at once as a bright red precipitate. When all had been added the solution was stirred for a further 45 minutes and then the solid was collected on a large Buchner funnel by suction and washed with copious quantities of water. After drying overnight *in vacuo* over silica gel the red powder was recrystallized from boiling ethanol to yield (9) as maroon felted needles [15.45 g, 57.4%; m.p. 159-161 °C (lit.[8] 162 - 163°C)]. (Found: C, 58.05; H, 4.1; N, 25.65%. Calc for $C_{13}H_{11}N_5O_2$: C, 58.0; H, 4.1; N, 26.0%.)

Any tendency to form tar was minimized by keeping the temperature well below 0°C, by waiting long enough for the nitrogen oxides to escape after diazotization, and by employing pure nitromethane and freshly distilled aniline.

3-Nitro-1,5-di(*p*-tolyl)formazan (10)

This was prepared in the same way as (9). The solid *p*-toluidine (4-aminotoluene; 21.43 g; 0.020 mol) was crushed and dissolved in hydrochloric acid (60 cm^3) and water (100 cm^3) with heating. The hydrochloride salt precipitated on cooling, and the diazotization proceeded as before. A viscous tar developed on coupling, which solidified on standing overnight. The solid was filtered off and washed in the usual

way. Some tar collected on the stirrer shaft was extracted into chloroform; after evaporation of the solvent the residue was added to the solid filtered off and the whole was recrystallized from ethanol to yield the nitroformazan (10) as red felted needles of 1 - 2 cm length [9.30g, 31.3%; m.p. 159-162°C (lit.[8] 160-162°C)]. (Found: C, 60.55; H, 5.15; N, 23.2%. Calc. for $C_{15}H_{15}N_5O_2$: C, 60.6; H,5.05; N, 23.6%.)

3-Nitro-1,5-di(*m*-tolyl)formazan (11)

This was prepared in the same way as (9). A sticky oil developed initially on coupling, but this solidified after a further 4 hours stirring to give dark red needles of (11) after recrystallization from ethanol (4.34g, 14.8%; m.p. 155-157°C). (Found: C,60.65; H, 5.2; N, 23.4%. $C_{15}H_{15}N_5O_2$requires C, 60.6; H, 5.05; N, 23.6%.)

3-Nitro-1,5-di(*o*-tolyl)formazan (12)

This was prepared in the same way as (9), but again a tar formed which solidified after 4 hours stirring. Recrystallization as before gave long maroon needles of (12) [7.60g, 12.8%; m.p. 151-154°C (lit.[8] 153-154)]. (Found: C, 60.65; H, 5.1; N, 23.6%. Calc. for $C_{15}H_{15}N_5O_2$: C, 60.6; H, 5.05; N, 23.6%.)

3-Nitro-1,5-di(3,5-dimethylphenyl)formazan (13)

This was prepared in the same way as (9), but after coupling the solution was left overnight for complete precipitation. After recrystallization from a chloroform-ethanol mixture (13) was obtained as a brick-red powder (13.28 g, 40.8%; m.p. 143-145°C). (Found: C, 62.3; H, 5.95; N 21.3%. $C_{17}H_{19}N_5O_2$ requires C, 62.8; H, 5.85; N, 21.5%.)

3-Nitro-1,5-di(2,6-dimethylphenyl)formazan (14)

The same procedure as used for (9) was carried out. After coupling and stirring for several hours a small quantity of red oil was extracted into chloroform. After evaporation of the solvent the residue was taken up in the minimum amount of benzene and transferred to an alumina column. Elution with benzene gave an initial red band which was collected. After removal of the solvent by evaporation at room temperature the residue was recrystallized from ethanol to yield well-formed dark red needles of (14) (0.38 g, 1.2%; m.p. 117-200°C). (Found: C, 62.55; H, 5.9; N, 21.3%. $C_{17}H_{19}N_5O_2$ requires C, 62.8; H, 5.85; N, 21.5%).

Further attempts at this method of preparation of (14), in which the concentration of hydrochloric acid was increased, or in which HCl was replaced by sulphuric acid (to guard, by extensively protonating the amino group, against partial diazotization, self-coupling, and the formation of diazoamino compounds), or in which the diazotization was conducted at -20°C (to guard against partial hydrolysis of the diazonium salt to the corresponding phenol), also resulted in yields around 1%.

An alternative method of synthesis was attempted based upon Hodgson's method of isolation of the diazonium sulphate.[87,88] Sodium nitrite (1.85 g) was finely powdered and added to cold (0°C) concentrated sulphuric acid with vigorous stirring. The temperature of the mixture was slowly raised to 70°C until all the $NaNO_2$ had dissolved and was then cooled again to 0°C. A cold solution of 2,6-dimethylaniline (2.4 g) in glacial acetic acid (24 cm^3) was stirred into the $NaNO_2/H_2SO_4$ solution at 0°C. After stirring for 15 minutes at this temperature slow addition of diethyl ether (100 cm^3) resulted in precipitation of the diazonium

sulphate, which was filtered off and washed with an ether and glacial acetic mixture and then with ether; the salt was kept moist with ether to reduce the risk of detonation. An alkaline nitromethane solution prepared as usual (1.1 g CH_3NO_2 in 5 cm^3 ethanol added slowly to 0.5 g NaOH in 10 cm^3 water at 0°C) was added dropwise to a cold (0°C) solution of the diazonium sulphate in aqueous sulphuric acid buffered at pH 4.5 with sodium acetate. No coupling reaction occurred after 4 hours stirring at 0°C followed by a further 2 hours stirring at room temperature; the solution remained a clear yellow-green colour throughout.

3-Nitro-1,5-di(2,4,6-trimethylphenyl)formazan (15)

This was prepared in the same way as (9). The same extraction and chromatographic purification procedure as used for (14) gave well-formed needles of (15) (0.12 g, 0.4%; m.p. 122-124°C). (Found: C, 64.6; H, 6.7; N, 19.8%. $C_{19}H_{23}N_5O_2$ requires C, 64.6; H, 6.6; N, 19.8%.) Several variations of the conditions of synthesis analogous to those tried for (14) were also used in an attempt to improve the yield of (15), but the resultant yield was always less than 1%.

3-Nitro-1,5-di(*p*-isopropylphenyl)formazan (16)

This was prepared in the same way as (9) except that after coupling an oil formed which was extracted into chloroform. After evaporation of the solvent the residue was recrystallized from ethanol to give bright red flaky plates of (16) (2.12 g, 16.2%; m.p. 130-133°C). (Found: C, 64.7; H, 6.7; N, 19.35%. $C_{19}H_{23}N_5O_2$ requires C, 64.6; H, 6.6; N, 19.8%.)

3-Nitro-1,5-di(*p*-n-butylphenyl)formazan (17)

This was prepared in exactly the same way as (9) to give maroon plates of (17) (10.65 g, 28.0%; m.p. 126-127°C). (Found: C, 66.2; H, 7.3; N, 18.35%. $C_{21}H_{27}N_5O_2$ requires C, 66.1; H, 7.1; N, 18.4%.)

Isotopically enriched analogues of (9)

After several 'dummy runs' optimizing reaction conditions to obtain the largest possible yields from expensive isotopically enriched reactants, the following general procedure was adopted for making both the ^{13}C- and ^{15}N-labelled analogues of (9). The ^{13}C-nitromethane (91 atom-%) and ^{15}N-aniline (96 atom-%) were supplied by BOC Prochem.

Sodium hydroxide (0.14 g) was dissolved in glass-distilled water (1 cm^3) in a 25 cm^3 beaker and cooled in an ice-salt bath to 0°C. A solution of nitromethane (0.22 g) in ethanol (1cm^3) was added slowly using a micro-pipette, the final drops being rinsed out with iced water (1 cm^3). A further 15 cm^3 of iced water was added to dissolve the white precipitate and the solution was kept at 0°C until used. Aniline (0.63 g) was dissolved in concentrated hydrochloric acid (3 cm^3) and water (4 cm^3) in a 100 cm^3 beaker and cooled to 0°C. A sodium nitrite solution (0.5 g in 1 cm^3 water) was added slowly with a micro-pipette to the vigorously stirred solution over 5 minutes. Sodium acetate (1.4 g) in water (4 cm^3) was then added slowly to the clear yellow diazotized solution. The alkaline nitromethane solution was then carefully added by micro-pipette, the last drops being washed out with iced water. The required nitroformazan separated out immediately as a bright red precipitate. After stirring for a further 30 minutes the solid was collected by filtration and washed with water. After drying overnight *in vacuo* over silica gel the red powder was recrystallized from ethanol. Red solid adhering to the Hirsch funnel, the stirring rod, and to glassware was washed off with chloroform and collected. After evaporation of the solvent the residue was also recrystallized from ethanol. The total yield of ^{13}C-labelled (9) after recrystallization was 0.50 g (54.8%; m.p. 160-161°C) and of ^{15}N-labelled (9) was 0.62 g (68.1%; m.p. 159-161°C).

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Deuteration of the nitroformazans (9) - (17)

The *N*-deuterated analogues of the nitroformazans (9) - (17) were made by precipitating the relevant nitroformazan (*ca.* 0.1 g) out of dimethylsulphoxide (1 cm^3) by the slow addition of D_2O (1 cm^3) with stirring. The precipitate was collected and the procedure was carried out three more times, after which the solid was dried *in vacuo* over silica gel. The ^1H n.m.r. spectra in $CDCl_3$ indicated virtually 100% deuteration by virtue of the complete absence of the N*H* resonance.

CHAPTER III

ISOMERISM IN S-METHYLDITHIZONES

CHAPTER III

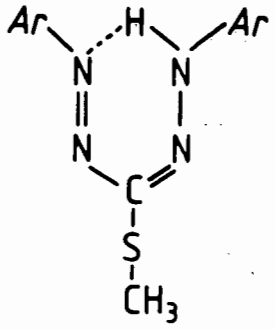
ISOMERISM IN *S*-METHYLDITHIZONES

1. Introduction

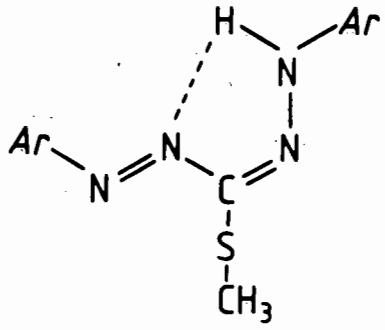
As mentioned in Chapter I, the classical method of determing the structure in potentially tautomeric systems such as dithizone [(1a) $\rightleftharpoons$ (1b)] is to compare the parent substance with derivatives in which the structure has been locked unambiguously by methylation into one or other of the possible tautomeric forms. This fails with dithizone. In 1953 Pel'kis reported that methylation of dithizone gave two isomers, PhN=N.C(SH)=N.N(Me)Ph and PhN=N.C(SMe)=N.NHPh (4), which were separated chromatographically and which were said to isomerize by the migration of a methyl group from nitrogen to sulphur.[165] Irving and Bell[28] however, obtained only a single pure *S*-methyl derivative (4) by methylating dithizone in alkaline solution with Me_2SO_4, by the action of MeI on silver dithizonate [Ag(HDz)], and (unambiguously) by the action of NaSMe upon 3-chloro-1,5-diphenylformazan [(2); $R^1 = R^2 = Ph$, $R^3 = Cl$]: Pel'kis later withdrew his earlier observations.[166]

Unfortunately, although a fresh solution of *S*-methyldithizone [3-methylthio-1,5-diphenylformazan; (4)] in, *e.g.*, chloroform is permanganate pink, with well-defined bands at 270 and 550 nm (ε_{550} = 1225 m^2 mol^{-1}), on standing in the dark at room temperature the colour changes to yellow, and the spectrum then shows bands at 280, 420, and 540 nm (ε_{420} = 1775 m^2 mol^{-1}), the band originally at 550 nm becoming less intense as the new band appears at 420 nm.[29] The process is kinetically first-order,[167] and is greatly accelerated by traces of acids and alkalis. The isomerism

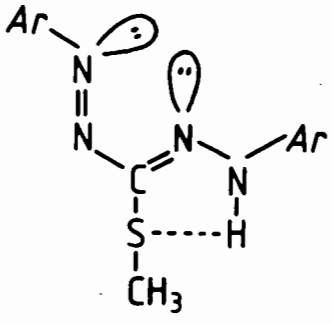
is reversed on illumination. Analogous effects appear with a number of *S*-alkylated dithizones [166,168,169] and with many other red formazans in general[30-33] which are converted to a yellow isomer on standing or on irradiation of solutions in appropriate solvents. As mentioned in the previous Chapter, *cis-trans* isomerism about the -N=N- bond or *syn-anti* isomerism about the :C=N- bond is thought to be involved.[29-33,69] Ignoring isomers which scale models show are unlikely to occur owing to serious steric crowding (*i.e.*, all the *cis*-configurations relative to the -N=N- double bond) leaves four isomers [(a), (d), (e), and (f)] as a



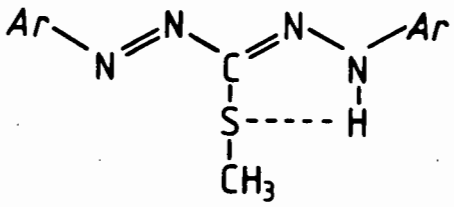
(a) *syn*,s-*cis*



(d) *syn*,s-*trans*



(e) *anti*,s-*cis*



(f) *anti*,s-*trans*

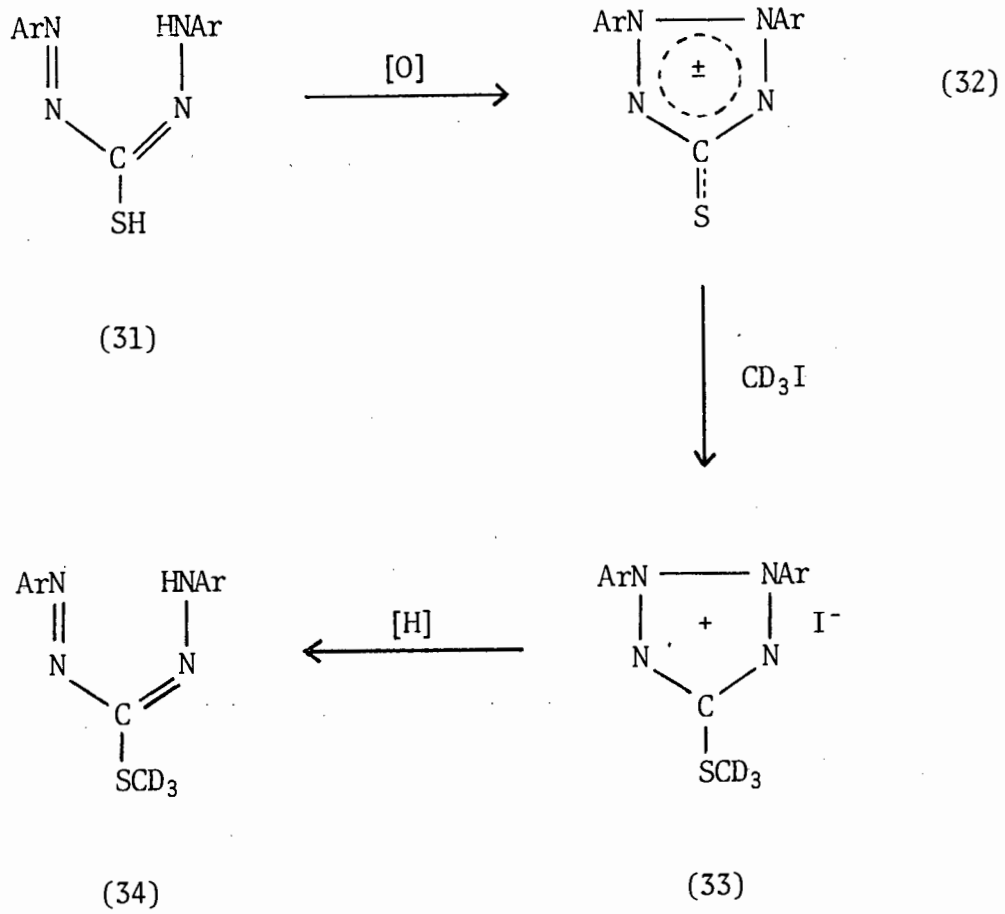
(4) : *Ar* = phenyl
(29) : *Ar* = *p*-tolyl
(30) : *Ar* = *o*-tolyl

result of *syn-anti* isomerization about the :C=N- double bond and isomerization about the C-N single bond (designated s-*cis* and s-*trans*). The alphabetic labels used here for the various isomers correspond with those used for the general formazan (2) in the previous Chapter; thus (a) $\rightleftharpoons$ (b) indicates rapid tautomerism between two equivalent structures and (c) is reserved for the postulated single mesomeric structure.

On concentration of solution of *S*-methyldithizone (4) (whether in the pink or yellow form) only the magenta-red solid (diffuse reflectance spectrum : $\lambda_{max.}$ 550 nm) is deposited. *X*-Ray crystallography[34] shows that the whole molecule is effectively planar and its *syn*,s-*trans* configuration can be represented by structure (4d).

The di(*p*-tolyl) (29) and di(*o*-tolyl) (30) homologues of (4) were prepared in this work by methylating the corresponding ring-substituted dithizones (synthesized for the work reported in Chapter IV) in alkaline solution with dimethylsulphate.[28,168] The corresponding -SCD_3 analogues (34) were synthesized by reacting CD_3I with the 2,3-diaryl-2*H*-tetrazolium-5-thiolate (32) obtained from oxidation of the corresponding substituted dithizone (31) and then reducing the resulting tetrazolium iodide (33) with alkaline dextrose.[59] *S*-Methyldithizone labelled at C(3) with ^{13}C and the analogue labelled at N(1) and N(5) with ^{15}N were also synthesized using this route from the parent labelled dithizone. Details are reported in the Experimental Section of this Chapter.

The *p*-tolyl homologue (29) crystallizes from ethanol as red needles which dissolve in chloroform to give a pink solution with a single band in the absorption spectrum at 550 nm (ε 1406 m^2 mol^{-1}). On leaving this solution to stand in the dark at room temperature the initial pink solution changed



to yellow-brown to give a new intense band at 425 nm with a concomitant decrease in the absorbance at longer wavelength, in exact analogy with the behaviour of the unsubstituted *S*-methyldithizone (4). Both compounds exhibit the same sequence of colour changes on isomerization and the rates of change are very easily affected by catalysts. As in the case of (4), the *p*-tolyl homologue (29) crystallizes as a dark red solid by concentration of solutions of either the pink or yellow isomer, and this solid redissolves to give a pink solution which again isomerizes to give an equilibrium mixture (isosbestic point 482 nm) of the pink and yellow forms. Addition of a trace of acetic acid converts the pink isomer to the yellow isomer instantly. These changes in the visible absorption

spectrum of the *p*-tolyl com0ound (29) are shown in Figure 12. From their similar solution behaviour and identical diffuse reflectance spectra ($\lambda_{max.}$ 550 nm) it may be presumed that the *p*-tolyl homologue (29) has the same solid state configuration as the parent *S*-methyldithizone (4), *viz syn*,s-*trans* (29d). The i.r. data reported in Section 3 of this Chapter (*q.v.*) support this assumption.

On the other hand, the *o*-tolyl homologue (30) crystallized from ethanol as yellow plates (diffuse reflectance spectrum: $\lambda_{max.}$ 423 nm). A fresh solution in chloroform was bright yellow and the absorption spectrum showed a well-defined peak at 420 nm (ε 2936 m^2 mol^{-1}). During several days in the dark the initially yellow solution in chloroform slowly formed a brown equilibrium mixture (isosbestic point 485 nm) with a pink isomer having a peak at 560 nm. Exposure of a fresh yellow solution to sunlight for 30 minutes gave the pure pink isomer, while addition of a trace of acetic acid caused immediate reversion to a red-brown equilibrium mixture. The preparation in the solid state of the pink isomer of the *o*-tolyl compound (30) was attempted by concentration of a solution of (30) in the pink form. The solid that separated was yellow-orange and identical with the initial solid product; it underwent the same sequence of colour changes (yellow $\longrightarrow$ brown $\longrightarrow$ pink) when it was redissolved in chloroform. Figure 13 shows these changes in the visible absorption spectrum of the *o*-tolyl compound (30) in chloroform.

It is clear that solutions in chloroform of (4), (29), or (30) which are more than a few hours old contain an equilibrium mixture of two isomers, pink and yellow. The nature of the pink isomer may be inferred from the crystal structure of the solid parent *S*-methyldithizone, whose diffuse reflectance spectrum and absorption spectrum in chloroform have the same

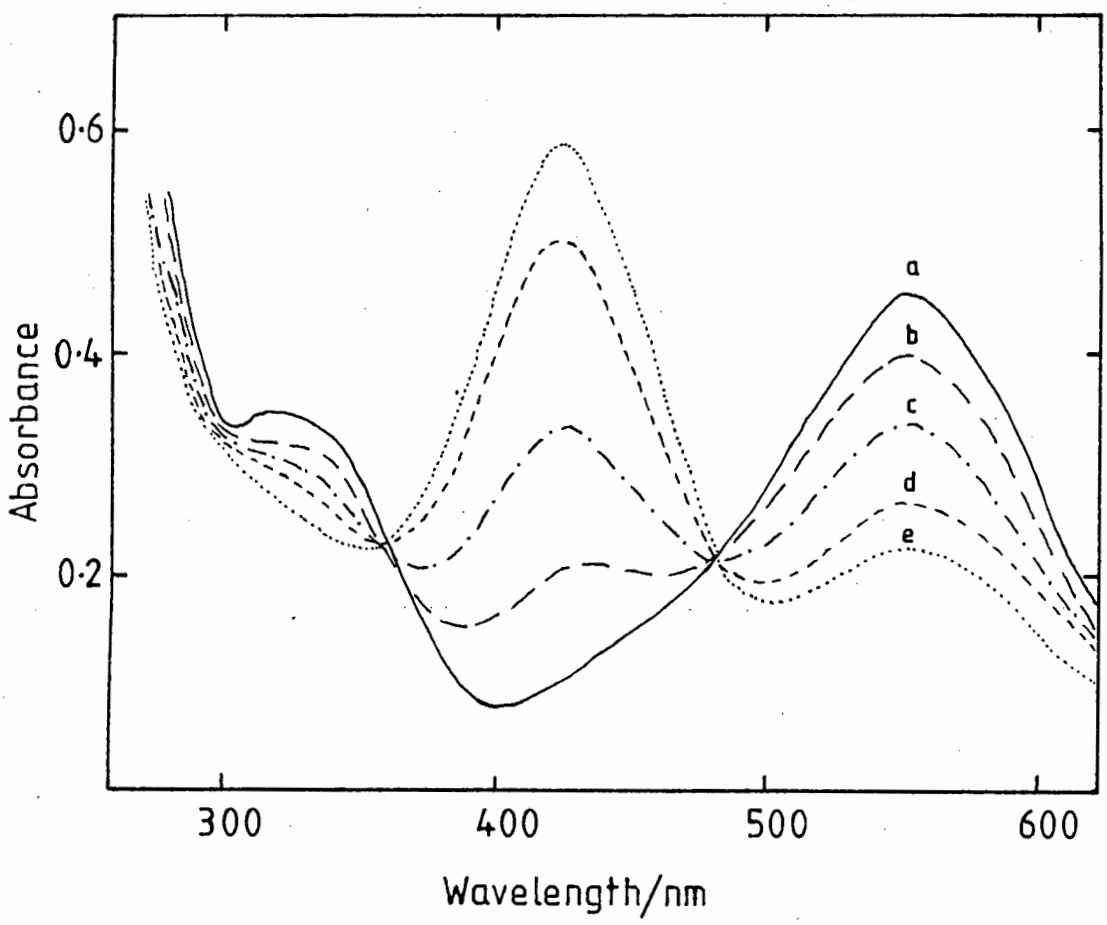


FIGURE 12 : Visible absorption spectrum of 3-methylthio-1,5-di(*p*-tolyl)-formazan (29) in chloroform solution (3.28×10^{-5} *M*) (a) pure pink isomer immediately after preparation, (b) after 1 hour, (c) after 6 hours, (d) after 24 hours, and (e) after addition of trace of acetic acid.

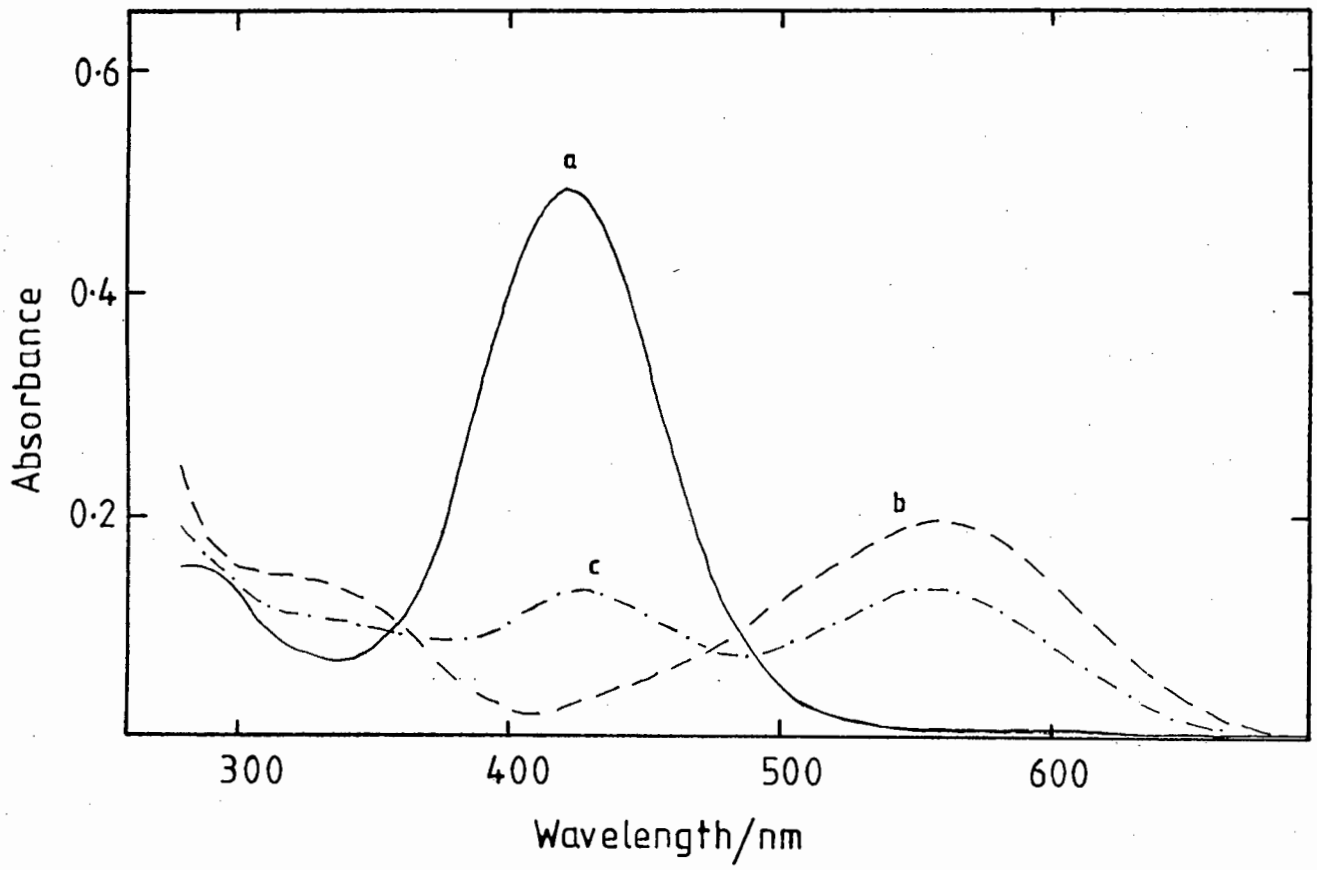


FIGURE 13 : Visible absorption spectrum of 3-methylthio-1,5-di(*o*-tolyl)-formazan (30) in chloroform solution (3.35×10^{-5} *M*) (a) pure yellow isomer immediately after preparation, (b) pink isomer after exposure to direct sunlight for 3 hours, and (c) after 2 days in the dark (equilibrium mixture of yellow and pink isomers).

$\lambda_{max.}$ (although this assumption of retainment of the solid state configuration upon dissolving in a solvent is not always valid, as will be seen in Section 3 of this Chapter). The chance discovery that the *o*-tolyl homologue (30) gives the same two isomers in solution but crystallizes in the yellow form enables the nature of the red $\rightleftharpoons$ yellow isomerism found in *S*-alkyldithizones to be finally elucidated, firstly by an X-ray crystallographic study of the *o*-tolyl homologue, and then by i.r. and n.m.r. spectroscopic studies on the pink and yellow forms of (4), (29), and (30) in solution.

2. Crystal and molecular structure of 3-methylthio-1,5-di(*o*-tolyl)formazan

The instruments and experimental methods used in this study were the same as those used and described in Chapter II, and their description will not be repeated here unless necessary.

Crystal and intensity data

An established route to 3-thio-1,5-diphenylformazan [(1), dithizone][3] was used to obtain 3-thio-1,5-di(*o*-tolyl)formazan, which was then reacted with dimethylsulphate to give the *S*-methylated product (30).[28] Details are reported in the Experimental Section of this Chapter. After purification by chromatography (alumina/benzene), the *o*-tolyl compound (30) was crystallized from ethanol as yellow-orange prismatic plates, m.p. 130-133°C (decomp.) (Found: C, 64.3; H, 6.0; N, 18.7%. Calc. for $C_{16}H_{18}N_4S$: C, 64.4; H, 6.1; N, 18.8%).

The density of the crystals was determined by the flotation method in aqueous potassium iodide. The density (D_m) was read off a nomogram as 1.29 g cm^{-3}.

Preliminary cell dimensions and space group symmetry were determined from oscillation and Weissenberg photographs. All the crystals were very thin plates and a single crystal of dimensions 0.5 x 0.4 x 0.05 mm was used for data collection. Accurate cell dimensions were obtained by least-squares from the settings of 25 high-order reflections measured on the Philips PW 1100 four circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The final cell parameters are given in Table 17 and using these and the measured density it was

TABLE 17 : CRYSTAL DATA

Molecular formula	: $C_{16}H_{18}N_4S$		
Molecular mass	: 298.40 g mol^{-1}		
Space group	: $P2_1/n$		
a = 7.993(4) Å		D_m = 1.29 g cm^{-3}	
b = 20.910(9) Å		D_c = 1.25 g cm^{-3}	for Z = 4
c = 10.154(5) Å		μ(Mo-K_α) = 1.63 cm^{-1}	
β = 110.43(5)°		$F(000)$ = 632	
V = 1590.4 Å^3			

calculated that there are four molecules in the unit cell. The conditions for non-extinction of reflections were found to be:

hkl : no conditions

$h0l$ $h + l = 2n$

$0k0$: $k = 2n$.

These conditions determine the space group uniquely as $P2_1/n$. This is a non-standard setting and is not listed in *International Tables for* X-*Ray crystallography*.[101] The space group $P2_1/n$ is the same as $P2_1/c$ except for a different choice of the c-axis. This space group was also found in the structure solved in the previous Chapter, where Figure 3 shows the relationship between unit cells with space groups $P2_1/n$ and $P2_1/c$.

Intensity data were collected by the ω - 2θ scan technique (scan width 0.5°θ, scan speed 0.01°θs^{-1}) in the range $3 \leqslant \theta \leqslant 20°$. Background was established as a function of θ from counting at the systematic absences and then subtracted. The intensities of three reference reflections monitored after every 68 measured reflections remained constant to within

±1% of their mean values. 1542 reflections were collected; with the criterion $I_{rel} > 2\sigma(I_{rel})$ for an observed reflection and omitting systematic absences, 1319 unique reflections remained which were employed in the analysis. Lorentz-polarization corrections were applied but correction for absorption was not deemed necessary. Table 17 summarizes the crystal data.

Solution and refinement of the structure

The structure was solved by weighted multisolution tangent refinement[170,171] applied to 307 reflexions with $|E| > 1.1$ using the *SHELX76* program system.[107] The iteration was begun with nine hand-selected reflections (Table 18). The first three were used to define the origin and were kept constant while the other six were treated as symbolic phases and allowed to assume the values 0 or π radians, giving a total of 64 phase permutations. After a number of cycles of weighted tangent refinement for each, eight E maps were calculated and ranked according to the reliability index R_A.[172] The highest ranking solution (R_A 0.121) appeared to give the positions of all but one of the heavy atoms, but attempts at refinement of the structure based on these positions failed. Further inspection of the E maps showed that several maps gave two shifted molecules and attempts at refining either of the individual molecules, or using the Patterson map to seek prominent vectors which would dictate appropriate shifts of the molecule, failed. The strucutre was finally solved by taking the 'average structure' of two shifted molecules given by an E map, as shown in Figure 14, the missing peaks being inferred from the geometry of the molecule.[173] This correctly yielded all but three of the heavy atom positions; these were found in subsequent difference maps. The vector between the two molecules equally displaced

TABLE 18 : REFLECTIONS USED IN THE STARTING SET WITH ALLOWED PHASES

h	k	l	E	ϕ/rad
2	13	4	4.541	0
1	13	5	4.153	0
-3	7	6	3.834	0
2	9	6	3.512	0, π
-1	13	1	3.315	0, π
0	4	2	2.994	0, π
1	4	1	2.978	0, π
1	8	3	3.717	0, π
1	5	1	2.828	0, π

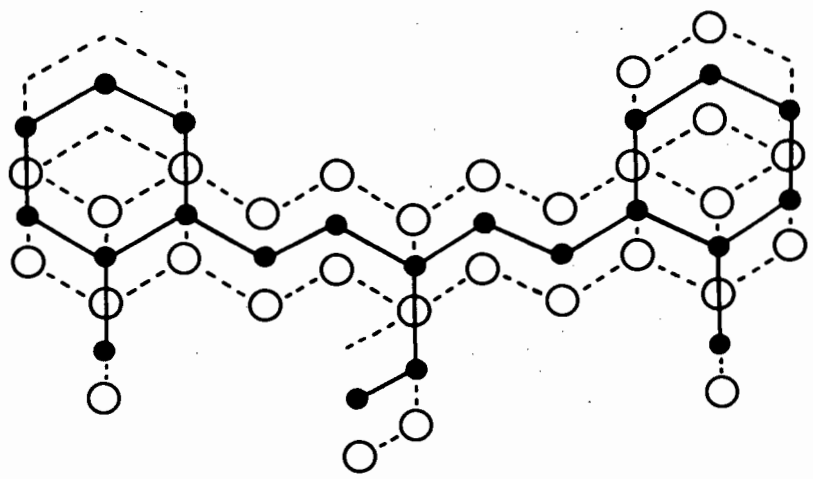


FIGURE 14 : Projection on the least-squares plane through peaks in the E map. The two shifted molecules are shown as open circles (not all atoms appear) and the 'average structure' as full circles.

in opposite directions from the correct position turns out to be a prominent vector in the correct structure, where it comprises contributions from six C-C vectors and the S-C bond vector. This shift vector has additional importance because it is perpendicular to a 2_1 axis.[174]

The final full-matrix least-squares refinement was carried out with all the heavy atoms treated anisotropically, as was done for *S*-methyldithizone (4) itself.[34] The aromatic and methyl hydrogen atoms were constrained to ride at 1.08 Å from their corresponding parent carbon atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as two single parameters which refined to U = 0.103(6) (aromatic H) and 0.142(8) Å^2 (methyl H). The imino proton, H(11), which had been revealed in a previous difference electron density map, was fixed at 1.00(1) Å from N(11) and its temperature factor was refined independently to U = 0.13(2) Å^2. The refinement converged to R = 0.064 and $R_w = \sum w^{\frac{1}{2}} ||F_o| - |F_c|| / \sum w^{\frac{1}{2}} |F_o|$ = 0.059 with the weighting scheme $w = (\sigma^2 F_o)^{-1}$ chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by an analysis of variance computed after the final cycle (Table 19). In the final cycle the mean e.s.d. in the parameters of the non-hydrogen atoms was greater than 100 times the average parameter shift. A final difference map showed no peaks greater than 0.2 e Å^{-3}. Complex neutral-atom scattering factors were taken from Cromer and Mann[109] for C, N, and S, and from Stewart, Davidson and Simpson[110] for H, with anomalous dispersion corrections from Cromer and Liberman.[111] Table 20 lists the observed and calculated structure factors, while the final atomic positional and thermal parameters are set out in Tables 21, 22, and 23.

TABLE 19 : ANALYSIS OF VARIANCE[a] FOR 3-METHYLTHIO-1,5-DI(*o*-TOLYL)FORMAZAN (30)

(a) As a function of sin θ

sin θ	0.00 - 0.16	0.16 - 0.20	0.20 - 0.23	0.23 - 0.25	0.25 - 0.27	0.27 - 0.29	0.29 - 0.30	0.30 - 0.32	0.32 - 0.33	0.33 - 0.35
N	144	144	147	121	130	174	91	184	93	91
V	125	114	82	95	93	89	84	91	63	52

(b) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.16	0.16 - 0.18	0.18 - 0.21	0.21 - 0.23	0.23 - 0.25	0.25 - 0.28	0.28 - 0.31	0.31 - 0.35	0.35 - 0.42	0.42 - 1.00
N	157	126	159	121	116	135	120	125	130	130
V	98	98	86	86	76	79	83	83	113	120

(c) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	186	155	160	164	156	173	160	165	1319
V	94	98	91	82	96	100	86	97	93

(d) As a function of |Miller index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	126	246	250	221	190	152	96	38	0	0	0	0	0	0	0
V	87	100	95	91	96	98	80	61	0	0	0	0	0	0	0

$\lvert k \rvert$	0	1	2	2	4	5	6	7	8	9	10	11	12	13	Rest
N	51	94	95	92	97	91	88	89	87	78	79	72	67	58	181
V	111	93	91	90	102	83	97	98	95	81	73	98	109	93	91

$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	106	202	209	193	172	150	117	88	61	21	0	0	0	0	0
V	101	112	101	96	92	83	72	72	74	54	0	0	0	0	0

[a] *N* = No. of reflections in the group

V = $100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections.

TABLE 20 : OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (30)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	26	-26	5	5	0	15	14	2	11	0	16	17	2	18	0	9	-9	-6	3	1	15	16
4	0	0	9	-10	6	5	0	7	6	3	11	0	6	5	3	18	0	4	-6	-5	3	1	19	21
6	0	0	35	35	0	6	0	68	-71	4	11	0	8	-8	1	19	0	3	-2	-4	3	1	2	2
2	1	0	2	-3	1	6	0	19	-22	5	11	0	5	-4	0	20	0	4	5	-3	3	1	10	-9
3	1	0	32	-31	2	6	0	27	-28	6	11	0	6	-6	-7	0	1	6	6	-2	3	1	23	24
4	1	0	12	11	4	6	0	16	17	0	12	0	3	0	-5	0	1	14	-14	-1	3	1	107	-106
5	1	0	3	-3	5	6	0	12	12	1	12	0	8	8	-3	0	1	60	60	0	3	1	31	32
6	1	0	16	16	6	6	0	9	-9	2	12	0	6	-6	1	0	1	50	-53	1	3	1	116	114
7	1	0	15	-14	1	7	0	3	-4	3	12	0	3	0	3	0	1	32	31	2	3	1	12	-12
1	2	0	45	47	2	7	0	5	-6	4	12	0	10	-9	5	0	1	25	25	3	3	1	12	12
2	2	0	74	-72	3	7	0	5	-3	5	12	0	8	-7	-7	1	1	8	-7	4	3	1	21	20
3	2	0	4	-5	4	7	0	11	-11	1	13	0	8	8	-6	1	1	15	-15	5	3	1	12	-11
4	2	0	21	-21	5	7	0	7	7	2	13	0	11	12	-5	1	1	5	4	-7	4	1	8	7
5	2	0	18	19	6	7	0	4	0	3	13	0	10	-11	-4	1	1	12	-11	-6	4	1	25	-28
6	2	0	12	11	0	8	0	19	-21	4	13	0	7	-7	-3	1	1	3	2	-5	4	1	5	-3
7	2	0	7	7	1	8	0	5	7	5	13	0	4	3	-2	1	1	10	-9	-4	4	1	19	20
2	3	0	45	-44	2	8	0	32	33	0	14	0	10	11	1	1	1	21	21	-3	4	1	32	-34
3	3	0	3	4	3	8	0	13	-12	1	14	0	6	5	2	1	1	17	15	-2	4	1	23	-24
4	3	0	8	9	4	8	0	25	25	2	14	0	3	0	3	1	1	8	10	-1	4	1	2	1
5	3	0	13	12	5	8	0	5	-5	3	14	0	3	-2	5	1	1	7	-8	0	4	1	64	-63
6	3	0	14	15	6	8	0	13	-12	4	14	0	6	-5	6	1	1	20	-21	1	4	1	149	-148
7	3	0	5	5	1	9	0	5	-5	1	15	0	4	3	-7	2	1	11	-11	2	4	1	8	-6
0	4	0	12	-12	2	9	0	54	55	2	15	0	4	-2	-6	2	1	12	-12	3	4	1	44	-43
1	4	0	86	-92	3	9	0	4	4	3	15	0	13	-13	-5	2	1	13	-15	4	4	1	12	11
2	4	0	46	-46	4	9	0	24	-24	0	16	0	7	5	-4	2	1	14	15	5	4	1	4	0
3	4	0	13	-14	5	9	0	11	-10	1	16	0	5	-4	-3	2	1	23	23	6	4	1	10	-11
4	4	0	8	-8	0	10	0	14	-14	2	16	0	8	-8	-2	2	1	5	-4	-7	5	1	11	-12
5	4	0	22	22	1	10	0	13	14	3	16	0	4	1	-1	2	1	22	22	-6	5	1	19	21
6	4	0	3	-2	2	10	0	34	35	4	16	0	4	-2	2	2	1	22	22	-5	5	1	35	38
7	4	0	7	-6	3	10	0	7	7	1	17	0	7	7	3	2	1	40	39	-4	5	1	20	21
1	5	0	24	-23	4	10	0	8	8	2	17	0	8	9	4	2	1	4	5	-3	5	1	7	-7
2	5	0	12	-12	5	10	0	3	-3	3	17	0	5	-5	5	2	1	17	17	-2	5	1	5	-5
3	5	0	31	33	6	10	0	6	-6	0	18	0	4	-3	6	2	1	6	-5	-1	5	1	48	-49
4	5	0	4	4	1	11	0	3	1	1	18	0	7	-6	-7	3	1	15	-15	0	5	1	49	-50

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	5	1	125	129	0	8	1	13	-12	-1	11	1	12	14	2	14	1	7	-8	2	19	1	4	3
2	5	1	22	22	1	8	1	52	54	0	11	1	3	2	3	14	1	6	6	0	20	1	4	4
3	5	1	28	-25	2	8	1	10	-9	1	11	1	13	-12	4	14	1	4	3	-6	0	2	14	13
5	5	1	13	-12	3	8	1	3	-2	2	11	1	2	2	-5	15	1	3	-3	-4	0	2	29	-26
6	5	1	7	6	4	8	1	9	9	3	11	1	15	-16	-4	15	1	7	7	-2	0	2	4	-3
-7	6	1	8	8	5	8	1	3	-3	4	11	1	3	2	-3	15	1	5	-4	0	0	2	59	59
-6	6	1	4	2	-6	9	1	5	4	5	11	1	9	8	-2	15	1	6	-5	2	0	2	36	37
-5	6	1	6	2	-5	9	1	7	-5	-5	12	1	7	-6	-1	15	1	5	4	4	0	2	16	15
-4	6	1	37	40	-4	9	1	18	-18	-4	12	1	9	-8	0	15	1	9	-9	-7	1	2	10	-8
-3	6	1	40	-43	-3	9	1	21	-21	-3	12	1	6	5	1	15	1	7	-6	-6	1	2	8	-7
-2	6	1	4	-5	-2	9	1	25	-25	-2	12	1	8	7	2	15	1	8	-8	-5	1	2	21	20
-1	6	1	2	0	-1	9	1	11	13	-1	12	1	7	7	4	15	1	8	8	-4	1	2	29	-29
0	6	1	55	56	0	9	1	32	32	0	12	1	8	8	-4	16	1	7	7	-3	1	2	71	-68
1	6	1	6	5	1	9	1	12	12	1	12	1	11	-12	-3	16	1	4	0	-2	1	2	19	17
2	6	1	6	-5	2	9	1	15	-15	2	12	1	16	-17	-2	16	1	4	-1	-1	1	2	22	-23
3	6	1	29	-28	3	9	1	26	-27	3	12	1	10	9	-1	16	1	4	0	0	1	2	39	-38
6	6	1	7	-7	4	9	1	15	-14	5	12	1	7	-9	0	16	1	6	-4	1	1	2	50	48
-6	7	1	9	9	5	9	1	16	16	-5	13	1	5	-3	1	16	1	12	-11	2	1	2	14	-14
-5	7	1	9	9	-6	10	1	4	-3	-4	13	1	4	1	2	16	1	8	9	3	1	2	7	7
-4	7	1	10	-11	-5	10	1	6	5	-3	13	1	11	-11	3	16	1	3	0	4	1	2	6	5
-3	7	1	8	-8	-4	10	1	3	1	-2	13	1	19	19	-4	17	1	5	4	5	1	2	27	-29
-2	7	1	16	-18	-3	10	1	7	-9	-1	13	1	51	52	-3	17	1	6	-6	6	1	2	8	8
-1	7	1	29	-28	-2	10	1	10	10	0	13	1	12	-12	-2	17	1	7	7	-7	2	2	5	3
0	7	1	23	26	-1	10	1	6	6	1	13	1	5	3	-1	17	1	9	-8	-6	2	2	22	23
1	7	1	17	-17	0	10	1	16	16	2	13	1	7	-6	0	17	1	6	-5	-5	2	2	14	-14
2	7	1	8	9	1	10	1	19	20	3	13	1	9	-8	1	17	1	8	7	-4	2	2	4	4
3	7	1	16	-16	2	10	1	7	-7	4	13	1	11	11	2	17	1	5	-4	-3	2	2	48	-46
4	7	1	10	-10	3	10	1	4	4	5	13	1	14	14	-3	18	1	5	-5	-2	2	2	23	21
-6	8	1	4	1	4	10	1	7	7	-4	14	1	6	-6	-2	18	1	8	-7	-1	2	2	14	-14
-5	8	1	15	16	5	10	1	9	-10	-3	14	1	8	7	-1	18	1	4	-3	0	2	2	67	62
-4	8	1	7	6	-5	11	1	15	-15	-2	14	1	4	1	0	18	1	9	-9	1	2	2	24	23
-3	8	1	13	-14	-4	11	1	9	-8	-1	14	1	5	-2	1	18	1	6	-6	2	2	2	17	17
-2	8	1	26	-25	-3	11	1	4	-4	0	14	1	3	0	2	18	1	8	8	3	2	2	23	-23
-1	8	1	29	30	-2	11	1	19	20	1	14	1	10	-9	-1	19	1	7	-5	4	2	2	9	-10

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
5	2	2	4	2	-2	5	2	33	32	-6	8	2	16	-17	4	10	2	7	5	4	13	2	13	14
6	2	2	6	-5	-1	5	2	62	60	-5	8	2	18	19	5	10	2	5	-5	-5	14	2	4	2
-7	3	2	15	15	0	5	2	92	91	-4	8	2	15	14	-6	11	2	7	-6	-4	14	2	3	-1
-6	3	2	7	5	1	5	2	3	-5	-3	8	2	20	21	-5	11	2	4	2	-3	14	2	13	-13
-5	3	2	9	9	2	5	2	64	-63	-2	8	2	34	34	-4	11	2	7	7	-2	14	2	9	-9
-4	3	2	50	-50	3	5	2	8	9	-1	8	2	29	-30	-3	11	2	14	15	-1	14	2	3	0
-3	3	2	12	-12	5	5	2	12	12	0	8	2	43	-44	-2	11	2	4	-4	0	14	2	5	5
-2	3	2	57	52	6	5	2	15	14	1	8	2	11	11	-1	11	2	5	-6	1	14	2	9	9
-1	3	2	57	55	-7	6	2	3	3	2	8	2	31	31	0	11	2	20	-22	2	14	2	8	8
0	3	2	99	96	-6	6	2	15	-16	3	8	2	19	19	1	11	2	10	11	3	14	2	4	-3
1	3	2	68	-64	-5	6	2	14	14	4	8	2	16	15	2	11	2	21	21	4	14	2	7	-5
2	3	2	21	-22	-4	6	2	8	7	5	8	2	5	-4	3	11	2	3	2	-5	15	2	4	4
3	3	2	9	9	-3	6	2	17	-16	-6	9	2	7	6	4	11	2	10	9	-4	15	2	3	0
4	3	2	4	3	-2	6	2	27	28	-5	9	2	28	-28	-6	12	2	5	5	-3	15	2	9	-9
5	3	2	8	-9	-1	6	2	9	9	-4	9	2	6	-6	-5	12	2	5	3	-2	15	2	4	1
6	3	2	19	18	0	6	2	28	-28	-3	9	2	10	9	-4	12	2	4	0	-1	15	2	5	-4
-7	4	2	5	-5	1	6	2	14	-14	-2	9	2	6	5	-3	12	2	10	-9	0	15	2	3	0
-6	4	2	10	-9	2	6	2	19	-19	-1	9	2	4	4	-2	12	2	4	1	1	15	2	12	12
-5	4	2	5	-5	3	6	2	18	-18	0	9	2	32	-31	-1	12	2	7	-8	2	15	2	7	7
-4	4	2	23	-23	4	6	2	14	14	1	9	2	3	-2	0	12	2	4	3	3	15	2	5	-4
-3	4	2	24	-25	5	6	2	4	3	2	9	2	23	-23	1	12	2	6	5	4	15	2	6	7
-2	4	2	4	4	-6	7	2	5	3	3	9	2	4	4	2	12	2	6	-5	-3	16	2	10	-9
-1	4	2	36	33	-5	7	2	26	-27	4	9	2	4	0	3	12	2	7	6	-2	16	2	11	-10
0	4	2	146	-142	-4	7	2	9	-9	5	9	2	5	4	4	12	2	9	-8	-1	16	2	10	9
1	4	2	21	22	-3	7	2	14	15	-6	10	2	10	-10	5	12	2	9	-9	0	16	2	4	2
2	4	2	29	-28	-2	7	2	3	-3	-5	10	2	10	10	-5	13	2	7	5	1	16	2	8	-8
3	4	2	3	-4	-1	7	2	14	-13	-4	10	2	3	-1	-4	13	2	10	9	2	16	2	7	6
4	4	2	5	4	0	7	2	2	1	-3	10	2	11	11	-3	13	2	4	-1	-4	17	2	12	-11
6	4	2	11	-10	1	7	2	46	-49	-2	10	2	28	27	-2	13	2	32	32	-3	17	2	3	0
-7	5	2	8	8	2	7	2	18	-17	-1	10	2	11	-12	-1	13	2	14	-15	-2	17	2	5	-2
-6	5	2	20	21	3	7	2	7	-6	0	10	2	12	-12	0	13	2	3	2	-1	17	2	7	-6
-5	5	2	5	3	4	7	2	5	-5	1	10	2	23	-24	1	13	2	10	10	0	17	2	3	-1
-4	5	2	41	-43	5	7	2	9	8	2	10	2	9	9	2	13	2	7	5	1	17	2	8	-8
-3	5	2	19	18	6	7	2	6	7	3	10	2	24	25	3	13	2	4	-4	2	17	2	16	-16

TABLE 20 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	18	2	7	-7	2	2	3	6	-5	-1	5	3	4	-5	-3	8	3	8	-8	-5	11	3	5	-1
-1	18	2	6	6	3	2	3	3	-1	0	5	3	2	3	-2	8	3	9	-8	-4	11	3	4	1
0	18	2	8	7	4	2	3	18	18	1	5	3	7	8	-1	8	3	46	-46	-3	11	3	4	-4
1	18	2	4	-3	5	2	3	7	7	2	5	3	7	7	0	8	3	44	45	-2	11	3	17	17
2	18	2	13	-13	-7	3	3	10	-10	3	5	3	23	24	1	8	3	75	79	-1	11	3	21	22
-1	19	2	9	8	-6	3	3	4	-4	4	5	3	13	-12	2	8	3	16	-16	1	11	3	20	21
0	19	2	6	5	-5	3	3	2	0	5	5	3	3	2	3	8	3	6	6	2	11	3	4	1
-7	0	3	10	9	-4	3	3	4	-3	-6	6	3	7	-6	4	8	3	3	-1	3	11	3	6	-6
-5	0	3	40	-39	-2	3	3	23	23	-5	6	3	6	5	5	8	3	9	-9	-6	12	3	4	4
-3	0	3	117	103	-1	3	3	16	16	-4	6	3	14	14	-6	9	3	5	-3	-5	12	3	5	-3
-1	0	3	7	-6	0	3	3	30	28	-2	6	3	13	-13	-5	9	3	13	-12	-4	12	3	23	-24
1	0	3	10	9	1	3	3	16	-16	-1	6	3	29	-30	-4	9	3	6	6	-3	12	3	7	-7
3	0	3	48	49	2	3	3	11	-11	0	6	3	15	15	-3	9	3	13	-14	-2	12	3	4	0
5	0	3	8	9	3	3	3	24	23	1	6	3	4	3	-2	9	3	4	-4	-1	12	3	11	10
-7	1	3	8	-8	4	3	3	9	8	2	6	3	7	-7	-1	9	3	33	-32	0	12	3	18	18
-6	1	3	9	-8	-7	4	3	8	-8	3	6	3	4	-3	0	9	3	3	0	1	12	3	4	-2
-5	1	3	3	-2	-6	4	3	23	-23	4	6	3	7	6	1	9	3	59	-62	2	12	3	4	-2
-4	1	3	43	-42	-5	4	3	3	1	5	6	3	11	-9	2	9	3	5	5	3	12	3	5	-4
-3	1	3	8	9	-4	4	3	28	28	-7	7	3	7	-8	3	9	3	4	-3	4	12	3	10	-9
-2	1	3	21	20	-3	4	3	14	13	-6	7	3	14	-15	4	9	3	5	-5	-5	13	3	11	-11
-1	1	3	22	21	-2	4	3	19	-17	-5	7	3	15	16	5	9	3	3	-4	-4	13	3	4	-2
0	1	3	3	-4	-1	4	3	46	-46	-4	7	3	5	6	-6	10	3	13	13	-3	13	3	6	5
1	1	3	2	-3	0	4	3	22	-24	-3	7	3	14	13	-5	10	3	20	21	-2	13	3	14	14
2	1	3	19	-20	1	4	3	9	10	-2	7	3	33	-33	-4	10	3	18	-18	-1	13	3	14	14
3	1	3	32	32	2	4	3	15	14	-1	7	3	3	0	-3	10	3	7	-6	0	13	3	3	-2
-7	2	3	5	5	3	4	3	12	-11	0	7	3	45	-46	-2	10	3	8	8	1	13	3	4	3
-6	2	3	15	-16	4	4	3	8	8	1	7	3	29	-29	-1	10	3	25	-25	2	13	3	3	0
-5	2	3	20	-21	5	4	3	9	-8	2	7	3	38	38	0	10	3	6	7	3	13	3	12	13
-4	2	3	22	-19	-7	5	3	15	-15	3	7	3	5	6	1	10	3	22	22	4	13	3	3	3
-3	2	3	25	24	-6	5	3	10	10	4	7	3	10	-10	2	10	3	4	-4	-5	14	3	10	-9
-2	2	3	5	-4	-5	5	3	6	6	-7	8	3	5	-5	3	10	3	5	-5	-4	14	3	18	-17
-1	2	3	15	-15	-4	5	3	20	21	-6	8	3	29	31	4	10	3	5	-5	-3	14	3	8	9
0	2	3	22	-22	-3	5	3	29	28	-5	8	3	23	23	5	10	3	13	-13	-2	14	3	4	-2
1	2	3	27	-25	-2	5	3	5	4	-4	8	3	4	5	-6	11	3	4	3	-1	14	3	9	9

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	14	3	3	2	2	0	4	47	47	1	3	4	3	2	-1	6	4	26	-25	-1	9	4	3	-2
1	14	3	13	-12	4	0	4	7	-7	2	3	4	5	5	0	6	4	22	21	0	9	4	32	-33
2	14	3	4	2	-7	1	4	11	-10	3	3	4	9	9	1	6	4	14	15	1	9	4	13	-14
-5	15	3	6	-5	-6	1	4	9	9	-7	4	4	5	3	2	6	4	12	-12	2	9	4	3	1
-4	15	3	9	-9	-5	1	4	14	14	-6	4	4	6	6	3	6	4	7	-7	3	9	4	4	-3
-3	15	3	8	7	-4	1	4	3	-2	-5	4	4	5	4	4	6	4	5	4	-6	10	4	8	-7
-2	15	3	3	1	-3	1	4	3	-1	-4	4	4	7	6	-6	7	4	5	4	-5	10	4	-8	-7
-1	15	3	10	10	-2	1	4	16	-14	-3	4	4	52	-50	-5	7	4	16	-16	-4	10	4	3	2
0	15	3	6	-6	-1	1	4	48	-49	-2	4	4	31	-30	-4	7	4	4	-4	-3	10	4	30	31
1	15	3	7	7	0	1	4	5	6	-1	4	4	7	8	-3	7	4	4	4	-2	10	4	5	-4
2	15	3	13	-12	1	1	4	8	8	0	4	4	33	32	-2	7	4	10	-9	0	10	4	8	8
3	15	3	5	5	2	1	4	6	5	1	4	4	35	34	-1	7	4	3	1	1	10	4	21	-21
-3	16	3	7	4	3	1	4	13	13	2	4	4	3	-3	0	7	4	22	-22	2	10	4	11	-10
-2	16	3	13	12	4	1	4	8	-9	3	4	4	17	-17	1	7	4	3	1	3	10	4	13	14
-1	16	3	11	10	5	1	4	9	-9	4	4	4	17	-17	2	7	4	9	-9	-6	11	4	5	-4
0	16	3	18	-17	-7	2	4	10	10	5	4	4	4	-5	3	7	4	12	-11	-5	11	4	17	18
1	16	3	11	-11	-6	2	4	7	6	-6	5	4	19	19	4	7	4	11	-11	-4	11	4	8	7
2	16	3	9	8	-4	2	4	4	4	-5	5	4	17	-17	-7	8	4	9	9	-3	11	4	12	12
-3	17	3	7	7	-3	2	4	48	-46	-4	5	4	13	-13	-6	8	4	4	1	-2	11	4	6	5
-2	17	3	5	-4	-2	2	4	23	-24	-3	5	4	8	-8	-5	8	4	4	-2	-1	11	4	4	-3
-1	17	3	13	-12	-1	2	4	2	3	-2	5	4	3	3	-4	8	4	12	-12	0	11	4	20	-21
0	17	3	5	-5	0	2	4	33	-32	-1	5	4	7	7	-3	8	4	27	27	1	11	4	27	28
1	17	3	20	-20	1	2	4	25	25	0	5	4	62	61	-2	8	4	8	9	2	11	4	4	-2
2	17	3	9	9	2	2	4	26	27	1	5	4	17	-17	-1	8	4	6	8	3	11	4	6	-5
-2	18	3	5	5	3	2	4	15	-14	2	5	4	10	10	0	8	4	30	30	-6	12	4	8	-7
-1	18	3	10	11	4	2	4	10	-10	3	5	4	13	-13	1	8	4	8	-7	-5	12	4	25	-26
0	18	3	8	-8	5	2	4	3	-2	4	5	4	7	-6	2	8	4	18	-18	-4	12	4	11	11
1	18	3	22	-22	-6	3	4	14	14	5	5	4	11	11	3	8	4	3	-3	-3	12	4	8	8
-1	19	3	5	-4	-5	3	4	9	8	-7	6	4	5	4	4	8	4	3	2	-2	12	4	4	-4
0	19	3	5	6	-4	3	4	36	-33	-6	6	4	10	-9	-6	9	4	9	-8	0	12	4	3	3
-6	0	4	14	13	-3	3	4	41	39	-5	6	4	3	0	-5	9	4	14	-13	1	12	4	11	-9
-4	0	4	42	37	-2	3	4	4	-4	-4	6	4	14	-14	-4	9	4	4	4	2	12	4	17	-18
-2	0	4	26	-26	-1	3	4	27	26	-3	6	4	9	8	-3	9	4	5	4	3	12	4	3	0
0	0	4	4	-4	0	3	4	38	37	-2	6	4	8	-7	-2	9	4	5	-4	-5	13	4	16	15

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	13	-4	26	26	-3	0	5	21	-21	2	3	5	8	-8	-7	7	5	11	-12	-2	10	5	7	-8
-2	13	4	9	8	-1	0	5	51	51	3	3	5	19	19	-6	7	5	5	-4	-1	10	5	6	-8
-1	13	4	12	-11	1	0	5	37	-36	-7	4	5	6	-6	-5	7	5	4	4	0	10	5	6	6
0	13	4	12	-12	3	0	5	11	-11	-6	4	5	17	-17	-4	7	5	11	11	1	10	5	17	17
1	13	4	18	18	-7	1	5	4	-4	-5	4	5	4	-2	-3	7	5	3	3	2	10	5	10	10
2	13	4	45	48	-6	1	5	9	10	-4	4	5	13	-13	-2	7	5	38	-39	3	10	5	13	-13
3	13	4	4	-4	-5	1	5	4	-5	-3	4	5	14	-13	-1	7	5	14	-14	-6	11	5	11	11
-5	14	4	15	-16	-4	1	5	16	-14	-2	4	5	11	11	0	7	5	18	-18	-5	11	5	7	4
-4	14	4	14	13	-3	1	5	21	-19	-1	4	5	22	21	1	7	5	12	-13	-4	11	5	16	16
-3	14	4	4	-2	-2	1	5	3	4	0	4	5	28	-28	2	7	5	6	5	-3	11	5	24	-25
-2	14	4	8	-8	-1	1	5	17	18	2	4	5	6	-6	3	7	5	9	9	-2	11	5	11	11
-1	14	4	3	0	0	1	5	15	15	3	4	5	13	-13	-6	8	5	12	12	-1	11	5	7	-8
0	14	4	7	-6	1	1	5	17	-17	4	4	5	8	7	-5	8	5	13	13	0	11	5	14	14
1	14	4	7	6	2	1	5	19	-19	-7	5	5	4	-4	-4	8	5	3	3	1	11	5	20	20
2	14	4	21	20	3	1	5	3	1	-6	5	5	10	-10	-3	8	5	8	-8	2	11	5	5	2
-4	15	4	12	11	4	1	5	4	4	-5	5	5	12	-12	-2	8	5	11	11	3	11	5	9	-9
-3	15	4	8	-8	-7	2	5	6	5	-4	5	5	16	16	-1	8	5	13	-13	-5	12	5	4	2
-1	15	4	12	-11	-6	2	5	4	-3	-3	5	5	22	22	0	8	5	5	5	-4	12	5	6	4
0	15	4	6	-7	-5	2	5	7	-6	-2	5	5	20	-20	2	8	5	18	-20	-3	12	5	9	-8
1	15	4	10	-10	-4	2	5	12	-11	-1	5	5	24	22	3	8	5	6	5	-2	12	5	12	-12
2	15	4	11	11	-3	2	5	8	-8	0	5	5	5	6	-6	9	5	7	-7	-1	12	5	4	-3
-4	16	4	6	6	-2	2	5	15	15	1	5	5	14	-14	-5	9	5	22	23	0	12	5	3	-3
-3	16	4	3	1	-1	2	5	23	23	2	5	5	14	14	-4	9	5	20	21	1	12	5	9	-7
-2	16	4	4	-3	0	2	5	13	12	3	5	5	13	13	-3	9	5	16	-16	2	12	5	11	10
0	16	4	8	-6	2	2	5	9	-9	-7	6	5	7	-7	-2	9	5	3	-3	3	12	5	4	-4
1	16	4	5	-3	3	2	5	11	-10	-6	6	5	10	-9	-1	9	5	19	-18	-5	13	5	14	15
2	16	4	10	10	4	2	5	14	14	-4	6	5	3	1	0	9	5	14	-13	-4	13	5	13	-12
-2	17	4	11	-10	-5	3	5	10	-9	-3	6	5	11	12	1	9	5	3	1	-3	13	5	6	-6
0	17	4	5	-6	-4	3	5	18	17	-2	6	5	8	9	2	9	5	6	5	-2	13	5	4	3
1	17	4	7	7	-3	3	5	19	18	-1	6	5	6	5	3	9	5	20	-20	-1	13	5	4	4
-1	18	4	6	6	-2	3	5	19	-18	1	6	5	3	2	-6	10	5	7	7	0	13	5	8	7
0	18	4	8	-8	-1	3	5	26	24	2	6	5	4	2	-5	10	5	24	24	1	13	5	40	41
-7	0	5	19	20	0	3	5	23	23	3	6	5	16	16	-4	10	5	18	18	2	13	5	10	-9
-5	0	5	12	-11	1	3	5	23	-22	4	6	5	4	3	-3	10	5	10	-10	-4	14	5	5	-3

TABLE 20 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	14	5	6	-5	0	2	6	21	-21	-3	6	6	8	-7	-3	10	6	9	8	-4	1	7	5	-5
-2	14	5	7	-7	1	2	6	14	14	-2	6	6	4	3	-2	10	6	4	3	-2	1	7	9	9
-1	14	5	9	9	2	2	6	12	11	-1	6	6	14	-14	-1	10	6	7	6	0	1	7	5	6
0	14	5	7	-6	-6	3	6	12	11	0	6	6	23	23	0	10	6	3	2	2	1	7	6	-4
1	14	5	13	12	-5	3	6	9	-9	2	6	6	8	-7	1	10	6	3	1	-6	2	7	8	8
-4	15	5	16	-16	-4	3	6	16	15	3	6	6	5	-5	2	10	6	29	-29	-5	2	7	6	5
-3	15	5	4	-4	-3	3	6	8	8	-6	7	6	4	3	-5	11	6	17	16	-4	2	7	11	-10
-2	15	5	4	4	-2	3	6	33	-33	-5	7	6	3	-1	-4	11	6	7	-6	-3	2	7	17	-17
1	15	5	9	10	-1	3	6	9	8	-4	7	6	4	-1	-2	11	6	12	12	-2	2	7	16	17
-2	16	5	5	5	0	3	6	19	19	-3	7	6	49	-50	-1	11	6	10	10	0	2	7	15	15
-1	16	5	5	4	1	3	6	4	-4	-1	7	6	11	10	0	11	6	9	9	2	2	7	7	-7
0	16	5	5	-6	2	3	6	17	17	0	7	6	7	7	1	11	6	9	10	3	2	7	12	-11
-6	0	6	12	-11	3	3	6	9	9	1	7	6	3	-2	2	11	6	14	-14	-6	3	7	4	-4
-4	0	6	19	18	-7	4	6	4	-5	2	7	6	3	0	-5	12	6	8	-8	-5	3	7	18	-18
-2	0	6	5	6	-5	4	6	13	12	3	7	6	13	-12	-4	12	6	10	10	-4	3	7	4	-3
0	0	6	67	-67	-4	4	6	14	-14	-6	8	6	14	14	-3	12	6	4	3	-3	3	7	5	3
2	0	6	5	5	-3	4	6	21	-22	-5	8	6	4	0	-2	12	6	6	6	-2	3	7	8	7
4	0	6	6	7	-2	4	6	7	8	-4	8	6	23	-24	-1	12	6	4	-5	-1	3	7	16	16
-6	1	6	3	3	-1	4	6	14	-15	-3	8	6	15	15	0	12	6	7	-5	0	3	7	5	-4
-5	1	6	8	7	1	4	6	17	17	-2	8	6	15	16	1	12	6	4	-1	1	3	7	18	-18
-4	1	6	9	8	2	4	6	6	6	-1	8	6	4	-3	-3	13	6	6	5	2	3	7	8	8
-3	1	6	20	19	3	4	6	7	7	0	8	6	19	18	-2	13	6	4	3	-6	4	7	8	9
-2	1	6	12	-13	-6	5	6	10	10	1	8	6	5	-4	0	13	6	7	7	-5	4	7	11	-11
-1	1	6	6	-7	-5	5	6	3	-2	2	8	6	15	-14	1	13	6	3	-2	-4	4	7	19	-18
0	1	6	8	-8	-4	5	6	6	-5	3	8	6	4	4	-1	14	6	3	-4	-3	4	7	13	14
1	1	6	8	-8	-3	5	6	19	-20	-5	9	6	18	18	1	14	6	4	-3	-2	4	7	18	18
2	1	6	6	6	-2	5	6	8	-8	-4	9	6	18	-18	-1	15	6	9	-10	0	4	7	5	4
3	1	6	6	5	0	5	6	14	14	-3	9	6	11	-10	-5	0	7	10	10	1	4	7	9	9
4	1	6	3	-4	1	5	6	12	12	-2	9	6	5	-4	-3	0	7	15	-15	-6	5	7	5	-5
-5	2	6	17	16	2	5	6	4	4	-1	9	6	13	14	-1	0	7	5	6	-5	5	7	22	-24
-4	2	6	17	17	3	5	6	6	-5	0	9	6	5	4	1	0	7	3	1	-4	5	7	20	-21
-3	2	6	6	-6	-6	6	6	9	9	2	9	6	31	-31	3	0	7	6	-5	-3	5	7	22	23
-2	2	6	13	14	-5	6	6	7	7	-5	10	6	11	10	-6	1	7	17	16	-1	5	7	15	15
-1	2	6	7	6	-4	6	6	16	-17	-4	10	6	16	-16	-5	1	7	4	-2	1	5	7	17	-17

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	6	7	9	-9	-3	9	7	3	1	-4	1	8	15	15	-2	5	8	7	-8	-1	10	8	12	13
-4	6	7	36	-38	-2	9	7	5	5	-3	1	8	30	31	-1	5	8	10	-10	-3	11	8	5	4
-3	6	7	21	21	-1	9	7	9	-8	-2	1	8	10	-11	0	5	8	5	-4	-2	11	8	5	6
-2	6	7	5	4	0	9	7	5	-4	0	1	8	3	-3	-5	6	8	8	-10	-1	11	8	10	10
-1	6	7	3	-2	1	9	7	8	-7	1	1	8	8	-8	-4	6	8	4	3	-5	0	9	14	13
0	6	7	9	-8	-4	10	7	13	12	-6	2	8	13	-12	-3	6	8	3	-3	-3	0	9	18	-19
1	6	7	14	-14	-3	10	7	6	6	-5	2	8	4	1	-2	6	8	12	-13	-5	1	9	4	-3
2	6	7	13	-13	-2	10	7	10	-9	-4	2	8	4	3	0	6	8	8	7	-4	1	9	23	23
-6	7	7	3	-3	-1	10	7	5	-4	-3	2	8	31	33	1	6	8	10	-11	-3	1	9	12	-12
-5	7	7	3	1	1	10	7	9	-10	-1	2	8	4	4	-5	7	8	5	5	-2	1	9	11	-12
-4	7	7	16	-15	-5	11	7	5	6	0	2	8	6	-6	-4	7	8	3	-1	-4	2	9	9	10
-3	7	7	5	4	-4	11	7	5	5	-5	3	8	15	-15	-3	7	8	10	-10	-3	2	9	7	-7
-2	7	7	5	5	-3	11	7	3	1	-4	3	8	15	15	-2	7	8	4	-3	-2	2	9	11	12
-1	7	7	3	3	-2	11	7	13	14	-3	3	8	19	20	-1	7	8	6	-5	0	2	9	8	9
0	7	7	12	-12	-1	11	7	7	-6	-2	3	8	16	-16	1	7	8	8	7	-5	3	9	11	-11
1	7	7	7	-7	-4	12	7	6	7	-1	3	8	6	-7	-4	8	8	6	-7	-4	3	9	11	12
2	7	7	9	-10	-2	12	7	17	-17	0	3	8	14	-14	-3	8	8	3	-3	-3	3	9	3	4
-6	8	7	8	8	-1	12	7	6	-6	-5	4	8	4	4	-2	8	8	8	-8	-2	3	9	12	-13
-5	8	7	4	3	-3	13	7	9	-10	-4	4	8	4	0	-1	8	8	3	1	-4	4	9	10	-10
-4	8	7	4	0	-1	13	7	7	9	-3	4	8	5	5	0	8	8	8	8	-3	4	9	6	-7
-3	8	7	16	16	-2	14	7	7	-7	-2	4	8	5	-4	-4	9	8	5	-4	-2	4	9	4	5
-2	8	7	7	7	-6	0	8	16	-15	-1	4	8	7	-7	-3	9	8	9	-9	-4	5	9	15	-15
-1	8	7	8	-9	-4	0	8	33	34	0	4	8	7	6	-1	9	8	3	4	-2	5	9	4	4
1	8	7	10	-9	-2	0	8	6	-5	-5	5	8	11	-11	-4	10	8	3	-3	-4	6	9	9	-9
-5	9	7	3	2	0	0	8	14	-14	-4	5	8	18	18	-3	10	8	7	-7	-2	7	9	6	7
-4	9	7	12	12	-5	1	8	12	-11	-3	5	8	10	-9	-2	10	8	7	9					

TABLE 21 : FRACTIONAL ATOMIC COORDINATES (x 10^4) OF THE NON-HYDROGEN ATOMS WITH E.S.D.'S IN PARENTHESES

	x/a	*y/b*	*z/c*
C(1)	6710(8)	2076(3)	6972(6)
C(2)	8221(11)	2454(3)	7530(6)
C(3)	9562(10)	2451(3)	6994(8)
C(4)	9455(8)	2055(3)	5873(7)
C(5)	7973(8)	1672(3)	5281(5)
C(6)	6605(7)	1683(2)	5829(5)
N(7)	5008(5)	1322(2)	5274(4)
N(8)	4976(5)	945(2)	4283(4)
C(9)	3408(6)	596(2)	3704(5)
N(10)	3447(5)	229(2)	2687(4)
N(11)	2063(6)	-150(2)	2077(4)
C(12)	2055(7)	-541(2)	959(5)
C(13)	3453(6)	-526(2)	446(5)
C(14)	3400(7)	-911(3)	-675(6)
C(15)	1971(8)	-1311(3)	-1284(5)
C(16)	591(7)	-1325(3)	-761(5)
C(17)	594(6)	-942(2)	362(5)
S(18)	1535(2)	674(1)	4239(1)
C(19)	2419(7)	410(3)	6048(5)
C(20)	5247(8)	2087(3)	7588(6)
C(21)	-937(6)	-973(3)	914(5)

TABLE 22 : FRACTIONAL ATOMIC COORDINATES (x 10^3) OF THE HYDROGEN ATOMS[a]

	x/a	*y/b*	*z/c*
H(2)	834	276	841
H(3)	1071	276	744
H(4)	1053	205	546
H(5)	788	137	440
H(11)	99	-10	235
H(13)	458	-22	92
H(14)	448	-90	-108
H(15)	193	-161	-216
H(16)	-52	-164	-124
H(191)	132	36	643
H(192)	340	73	673
H(193)	302	-5	603
H(201)	391	212	682
H(202)	551	250	826
H(203)	536	166	821
H(211)	-190	-131	26
H(212)	-156	-51	87
H(213)	-46	-114	199

[a] Numbered according to the atom to which bonded.

TABLE 23 : ANISOTROPIC THERMAL-MOTION PARAMETERS ($Å^2 \times 10^3$)[a] WITH E.S.D.'S IN PARENTHESES

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	84(4)	51(3)	59(4)	6(3)	14(3)	-1(3)
C(2)	115(5)	61(4)	69(4)	-8(3)	13(4)	-9(4)
C(3)	104(6)	100(5)	87(6)	8(4)	7(4)	-39(4)
C(4)	83(5)	112(5)	87(5)	22(4)	26(4)	-24(4)
C(5)	73(4)	93(4)	55(4)	5(3)	24(3)	-19(4)
C(6)	68(4)	56(3)	43(3)	0(3)	12(3)	-5(3)
N(7)	68(3)	54(3)	50(3)	-3(2)	18(2)	0(2)
N(8)	67(3)	62(3)	55(3)	-10(2)	25(2)	-4(2)
C(9)	54(3)	67(4)	51(3)	-7(3)	22(3)	-1(3)
N(10)	64(3)	58(3)	54(3)	-8(2)	28(2)	-1(2)
N(11)	59(3)	64(3)	57(3)	-10(2)	25(2)	-5(2)
C(12)	66(4)	47(3)	46(3)	-3(3)	22(3)	0(3)
C(13)	67(4)	68(4)	62(4)	-5(3)	32(3)	-3(3)
C(14)	78(4)	77(4)	68(4)	-8(3)	36(3)	-2(3)
C(15)	90(4)	77(4)	61(4)	-13(3)	34(4)	-2(4)
C(16)	73(4)	72(4)	59(4)	-11(3)	19(3)	-9(3)
C(17)	60(4)	54(3)	53(3)	4(3)	16(3)	3(3)
S(18)	56(1)	102(1)	67(1)	-14(1)	26(1)	7(1)
C(19)	75(4)	121(5)	73(4)	10(4)	37(3)	-2(3)
C(20)	106(5)	78(4)	75(4)	-17(3)	37(4)	5(4)
C(21)	61(3)	85(4)	72(4)	0(3)	30(3)	-5(3)

[a] In the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with SHELX76 (data reduction, structure solution and refinement),[107] XANADU (molecular geometry),[117] and PLUTO (illustrations).[118]

Molecular structure

The molecular structure and atomic nomenclature are shown in Figure 15; the numbering scheme is arbitrary but the same as that used by Preuss and Gieren[34] in their analysis of *S*-methyldithizone (4). Molecules in crystals of the *o*-tolyl homologue (30) differ from those in (4) in that the configuration about C(9)=N(10) is *anti* (30f) rather than *syn* (4d), the imino H(11) forming a hydrogen bond to S(18) rather than to N(8). The thiocarbazone chain chromophore is thus altered and the *o*-tolyl compound (30f) absorbs light of shorter wavelength (420 nm) than either (4d) or the *p*-tolyl compound (29d) (both 550 nm). While this work was in progress the *X*-ray crystal structure of 3-isopropylthio-1,5-diphenylformazan (*S*-isopropyldithizone) was reported.[92] This compound also crystallizes in the open *anti*,s-*trans* configuration ($\lambda_{max.}$ 430 nm) and will provide supporting evidence in the elucidation of the isomerism found in these compounds.

Bond lengths and angles for the *o*-tolyl compound (30) are given in Figure 16 for two molecules which are related to each other by a centre of symmetry. Tables 24 and 25 list the bond lengths and angles. The calculated bond lengths reveal a marked delocalization of π-electrons within the N-N-C-N-N chain and with the *o*-tolyl rings. While the formal double bonds C(9)=N(10) (1.30 Å) and N(7)=N(8) (1.27 Å) are clearly extended in comparison with isolated double bonds, the formal single

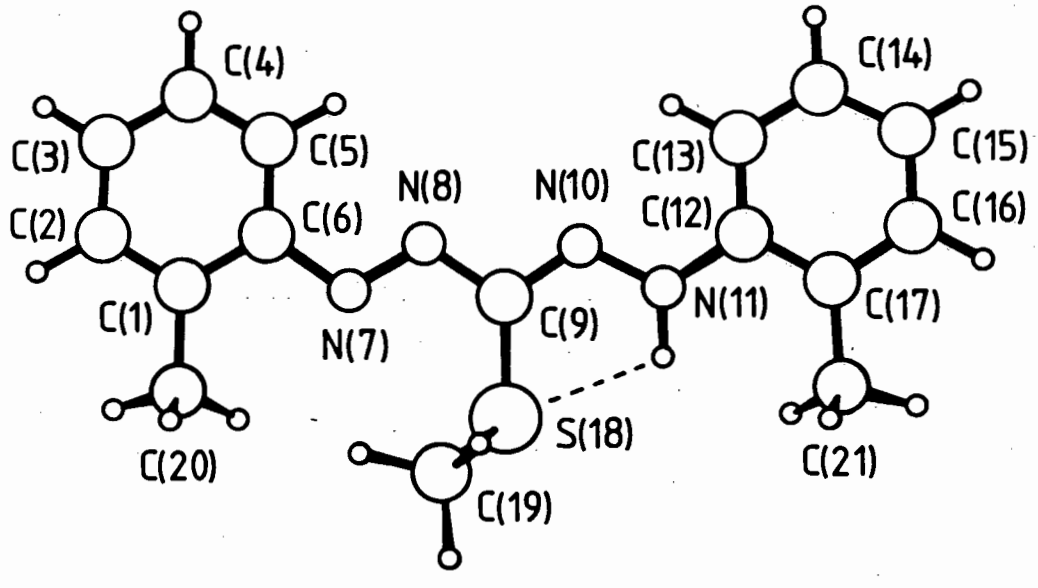


FIGURE 15 : Molecular structure and atomic nomenclature of 3-methylthio-1,5-di(*o*-tolyl)formazan (30). Hydrogen atoms are numbered according to the atom to which they are bonded. The dashed line indicates a hydrogen bond.

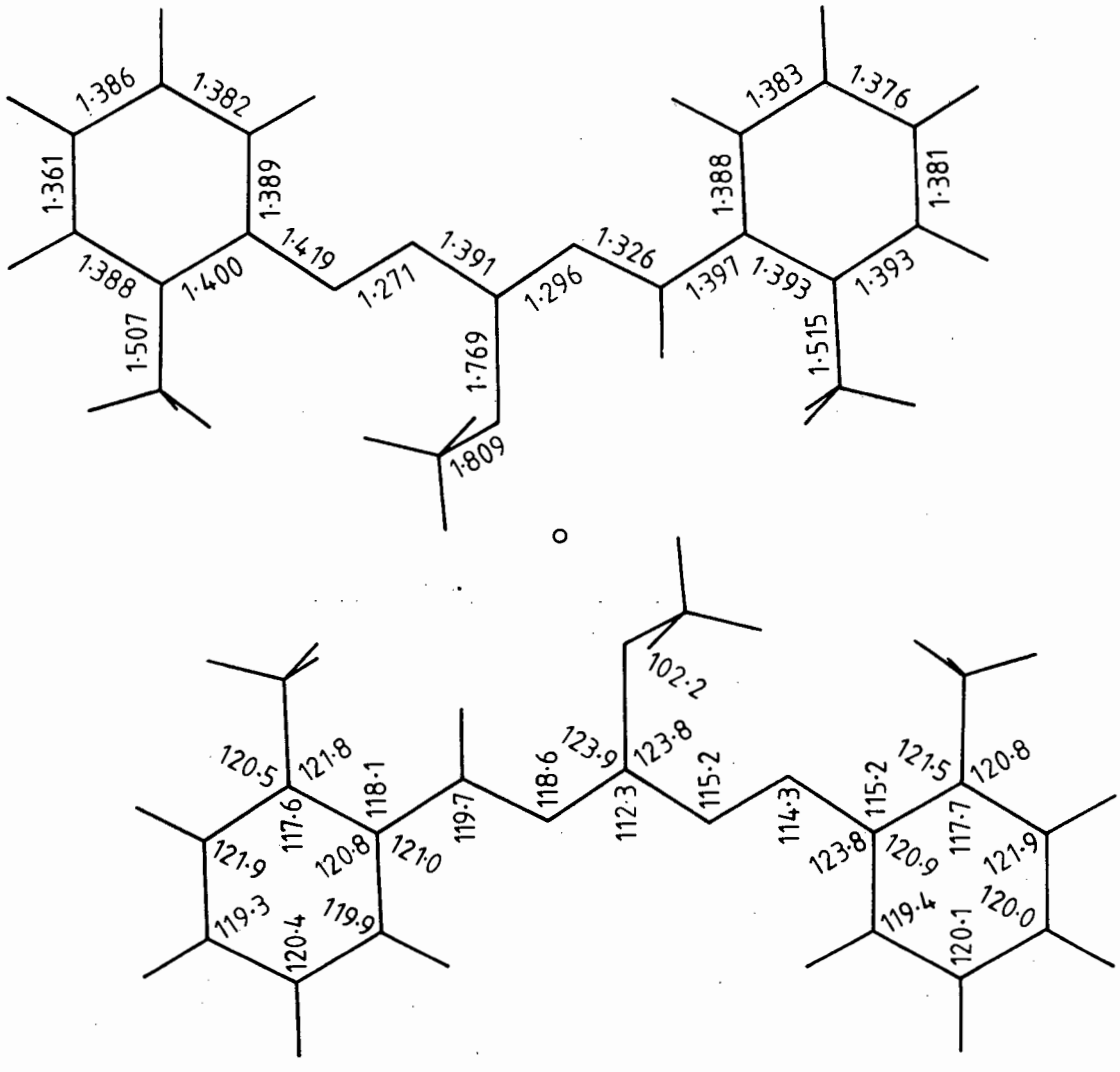


FIGURE 16 : Two molecules related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s are 0.006 - 0.008 for C-C and 0.004 - 0.006 Å for C-N, C-S, and N-N), while the lower molecule gives the bond angles (°; e.s.d.'s are 0.2 - 0.6°).

TABLE 24 : BOND LENGTHS (Å) WITH E.S.D.'S IN PARENTHESES

C(1) - C(2)	1.388(7)
C(1) - C(6)	1.400(6)
C(1) - C(20)	1.507(7)
C(2) - C(3)	1.361(8)
C(3) - C(4)	1.386(8)
C(4) - C(5)	1.382(7)
C(5) - C(6)	1.389(6)
C(6) - N(7)	1.419(6)
N(7) - N(8)	1.271(4)
N(8) - C(9)	1.391(5)
C(9) - S(18)	1.769(5)
S(18) - C(19)	1.809(5)
C(9) - N(10)	1.269(5)
N(10) - N(11)	1.326(5)
N(11) - C(12)	1.397(5)
C(12) - C(13)	1.388(6)
C(13) - C(14)	1.383(6)
C(14) - C(15)	1.376(6)
C(15) - C(16)	1.381(6)
C(16) - C(17)	1.393(6)
C(17) - C(12)	1.393(6)
C(17) - C(21)	1.515(6)
N(11) - H(11)	1.00(1)[a]
All C - H bond lengths	1.08[b]

[a] Constrained bond length.

[b] Fixed bond lengths.

TABLE 25 : BOND ANGLES (°) WITH E.S.D.'S IN PARENTHESES

C(1) - C(2) - C(3)	121.9(6)
C(2) - C(3) - C(4)	120.0(6)
C(3) - C(4) - C(5)	120.1(6)
C(4) - C(5) - C(6)	119.4(5)
C(5) - C(6) - C(1)	120.9(5)
C(6) - C(1) - C(2)	117.7(5)
C(2) - C(1) - C(20)	120.8(6)
C(6) - C(1) - C(20)	121.5(5)
C(1) - C(6) - N(7)	115.2(5)
C(5) - C(6) - N(7)	123.8(5)
C(6) - N(7) - N(8)	114.3(4)
N(7) - N(8) - C(9)	115.2(4)
N(8) - C(9) - S(18)	123.8(4)
C(9) - S(18) - C(19)	102.2(2)
N(8) - C(9) - N(10)	112.3(4)
S(18) - C(9) - N(10)	123.9(4)
C(9) - N(10) - N(11)	118.6(4)
N(10) - N(11) - C(12)	119.7(4)
N(11) - C(12) - C(17)	118.1(4)
N(11) - C(12) - C(13)	121.0(5)
C(12) - C(13) - C(14)	119.9(5)
C(13) - C(14) - C(15)	120.4(5)
C(14) - C(15) - C(16)	119.3(5)
C(15) - C(16) - C(17)	121.9(5)
C(16) - C(17) - C(12)	117.6(4)
C(17) - C(12) - C(13)	120.8(4)
C(16) - C(17) - C(21)	120.5(5)
C(12) - C(17) - C(21)	121.8(5)

bonds C(9)-N(8) (1.39 Å) and N(10)-N(11) (1.33 Å) are noticeably shortened.[119-121] The π-electron delocalization is not, however, as extensive as was found for the *syn*,s-*cis* formazan chain of 3-nitro-1,5-di(2,6-dimethylphenyl)formazan (14) (Chapter II), and the formal single and double bonds are still clearly identifiable in this case (30). Similar N - N - C - N - N chain lengths were observed in *S*-methyldithizone (4),[34] *S*-isopropyldithizone,[92] and 3-carboxymethylthio-1,5-diphenylformazan.[96] The S-C lengths are of the expected magnitude and show that the electron delocalization found in the Ar-N-N-C-N-N-Ar (Ar = *o*-tolyl) chain does not extend to the sulphur atom: the C(9)-S(18) bond order is ~1.0.[10] The difference between C(9)-S(18) (1.77 Å) and S(18)-C(19) (1.81 Å) follows from the difference in hybridization of the two carbon atoms [C(9) sp^2, C(19) sp^3]. Bond distances and angles relating to the *o*-tolyl groups are generally satisfactory. The mean aromatic C-C distance in the two rings is 1.385(10) Å. The weakly electron-donating methyl groups on the *o*-tolyl rings increase the σ-electron density along the (Ar)C-CH_3 bond and cause the corresponding interior angles to close to 117.6 and 117.7° (Figure 16); similar distortion was found in the 2,6-dimethylphenyl groups of the *X*-ray structure reported in Chapter II.

Selected torsion angles and the parameters for several least-squares planes are given in Tables 26 and 27, respectively. If the *S*-methyl group is ignored the remainder of the molecule is remarkably planar. The largest deviation from the C-N-N-C-N-N-C plane is 0.018(4) Å, illustrating the expected planarity consequent on electron delocalization. The largest deviation from the least-squares plane calculated through all

TABLE 26 : SELECTED TORSION ANGLES (°)[a]

C(2)	-	C(1)	-	C(6)	-	N(7)	-178.1[b]
C(20)	-	C(1)	-	C(6)	-	N(7)	2.3
C(4)	-	C(5)	-	C(6)	-	N(7)	178.2
C(1)	-	C(6)	-	N(7)	-	N(8)	-176.7
C(5)	-	C(6)	-	N(7)	-	N(8)	5.0
N(11)	-	C(12)	-	C(13)	-	C(14)	-179.0
N(11)	-	C(12)	-	C(17)	-	C(16)	180.0
N(11)	-	C(12)	-	C(17)	-	C(21)	-1.4
N(10)	-	N(11)	-	C(12)	-	C(13)	-1.9
N(10)	-	N(11)	-	C(12)	-	C(17)	178.8
C(6)	-	N(7)	-	N(8)	-	C(9)	-178.7
N(7)	-	N(8)	-	C(9)	-	N(10)	180.0
N(7)	-	N(8)	-	C(9)	-	S(18)	1.9
N(8)	-	C(9)	-	N(10)	-	N(11)	177.4
S(18)	-	C(9)	-	N(10)	-	N(11)	-5.6
N(8)	-	C(9)	-	S(18)	-	C(19)	-63.6
N(10)	-	C(9)	-	S(18)	-	C(19)	119.6
C(9)	-	N(10)	-	N(11)	-	C(12)	178.7

[a] The torsion angle convention is that of Klyne and Prelog[124] and was defined in Table 12 (Chapter II).

o-Tolyl-ring torsion angles are all < 1.2° and are omitted.

[b] Estimated standard deviations are *ca.* 0.5°.

TABLE 27 : LEAST-SQUARES PLANES PARAMETERS

(a) Equations of least-squares planes expressed in orthogonalized space as $PI + QJ + RK = S$

Plane 1 : all non-hydrogen atoms

$0.5017I - 0.7331J + 0.4591K = 1.8117$

Plane 2 : all non-hydrogen atoms excluding C(19)

$0.4389I - 0.7325J + 0.5204K = 1.7023$

Plane 3 : C(6), N(7), N(8), C(9), N(10), N(11), C(12)

$0.4096I - 0.7306J + 0.5463K = 1.6833$

Plane 4 : *o*-tolyl ring C(1) - C(6), C(20)

$0.4521I - 0.7355J + 0.5047K = 1.7117$

Plane 5 : *o*-tolyl ring C(12) - C(17), C(21)

$0.4669I - 0.7262J + 0.5047K = 1.7462$

(b) Deviations (Å × 10^3) from planes. Atoms included in the calculation are marked by asterisks. All e.s.d.'s are < 0.008 Å.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(1)	-81*	34*	50	-3*	76
C(2)	-27*	27*	14	-1*	104
C(3)	60*	-5*	-71	-5*	113
C(4)	119*	-10*	-104	9*	119
C(5)	62*	-9*	-77	1*	87
C(6)	-39*	12*	-1*	-7*	64
C(20)	-173*	75*	149	6*	70
C(12)	-26*	11*	-7*	19	-3*
C(13)	58*	-26*	-99	9	3*
C(14)	112*	-39*	-141	16	1*
C(15)	89*	-10*	-87	37	-1*
C(16)	12*	34*	11	54	1*
C(17)	-51*	42*	49	41	-5*
C(21)	-125*	100*	166	68	5*
N(7)	-139*	-20*	-3*	-51	-4
N(8)	-31*	27*	18*	15	53
C(9)	-154*	-32*	-12*	-55	-40
N(10)	-57*	-1*	-11*	-6	3
N(11)	-102*	4*	17*	-8	-23
S(18)	-489*	-214*	-125	-273	-277
C(19)	979*	1310	1419	1236	1236

(c) Angles (°) between normals to planes. All e.s.d.'s are < 0.8°.

Planes 1 and 2	5.0	Planes 2 and 4	1.2
Planes 1 and 3	7.3	Planes 2 and 5	1.9
Planes 1 and 4	3.9	Planes 3 and 4	3.4
Planes 1 and 5	3.3	Planes 3 and 5	4.1
Planes 2 and 3	2.2	Planes 4 and 5	1.0

the non-hydrogen atoms of the molecule except the *S*-methyl atom, C(19), is only 0.214(6) Å [for S(18)], with C(19) projecting 1.310(8) Å above this plane. The torsion angle[124] ω[N(8)-C(9)-S(18)-C(19)] is -63.6(5)° and ω[N(10)-C(9)-S(18)-C(19)] is 119.6(5)°. The corresponding torsion angles in the *syn*,s-*trans* *S*-methyldithizone (4d)[34] are -5.7 and 173.0° and clearly the *S*-methyl group in the *anti*,s-*trans* *o*-tolyl compound (30f) projects above the plane of the plane of the molecule in order to avoid steric interaction with N(7) or N(11), whereas interaction with N(11) in the *syn* configuration of (4d) is impossible and in (4) the atoms N(10)-C(9)-S(18)-C(19) form a synplanar arrangement. The torsion angles (Table 26) emphasize the remarkable planarity of the remainder of (30); there are no other torsion angles between non-hydrogen atom sequences whose deviations from planarity (0 or 180°) are >75.6°. The difference in exterior angles at C(6) and C(12) [115.2 and 123.8° at C(6); 118.1 and 121.0° at C(12)] is the same as that in (4)[34] and is explained by the steric interaction of the *o*-tolyl rings with atoms in the N-N-C-N-N chain; non-bonded intramolecular distances are given in Table 28. The angle between the normals to each *o*-tolyl ring plane is nevertheless only 1.0(5)°. Similar reasoning explains the orientation of the *o*-tolyl methyl groups with respect to the thiocarbazone chain, steric interaction of C(20) with N(8) and of C(21) with N(10) being avoided in the configuration adopted.

Molecular packing

A projection of the packing in crystals of the *o*-tolyl compound (30) is shown in Figure 17. Pairs of molecules related by centres of inversion may be regarded as packing units and are stacked in alterante directions along *b*. Unlike the packing in (4) where many close contacts are reported,[34]

TABLE 28 : INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°)

(a) Selected intramolecular non-bonded distances. E.s.d.'s are *ca.* 0.01 Å.

C(20)···N(7)	2.79
C(19)···N(7)	3.11
S(18)···N(7)	2.93
C(21)···N(11)	2.85
S(18)···N(11)	2.94
C(5) ···N(8)	2.72
C(13)···N(10)	2.77

(b) Intramolecular hydrogen bonding data

N(11)···S(18)	2.94(1)
N(11) - H(11)	1.00(1)[a]
H(11)···S(18)	2.42(5)
N(11) - H(11)···S(18)	97(4)
H(11) - N(11) - N(10)	118(3)
H(11) - N(11) - C(12)	122(3)

[a] Constrained bond length.

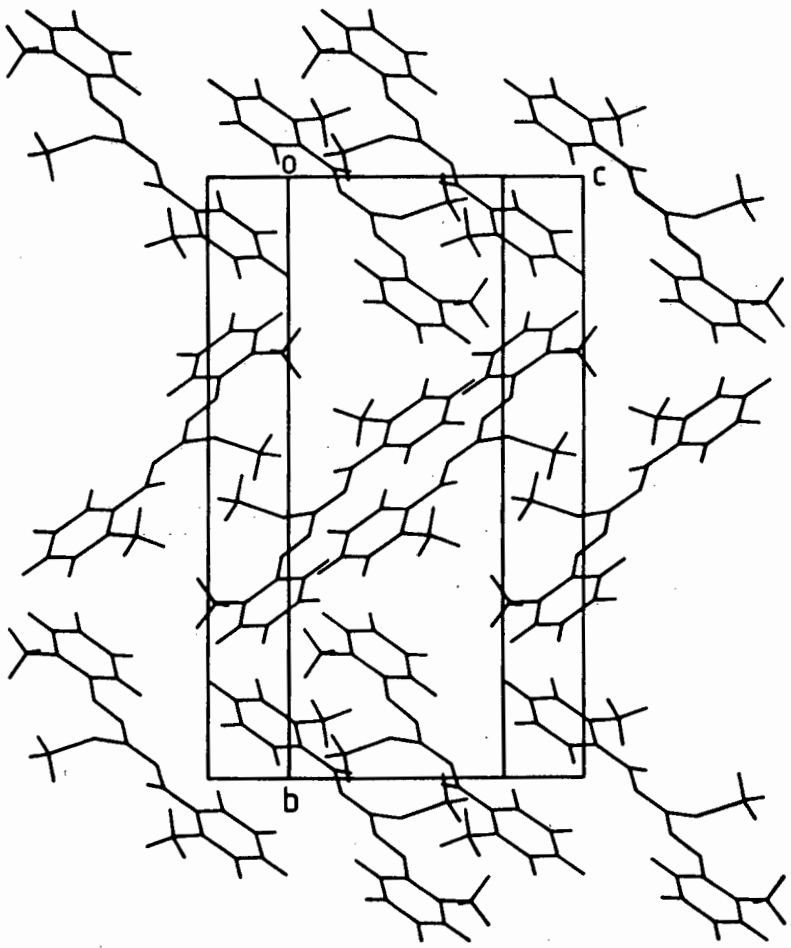


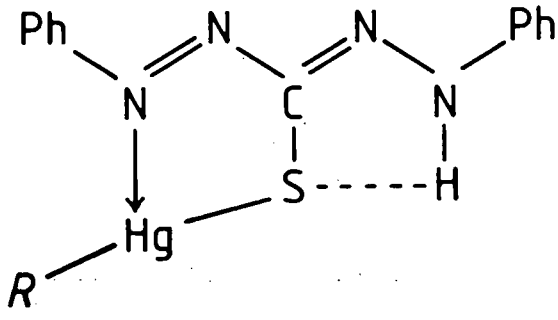
FIGURE 17 : A projection of the molecular packing of (30) viewed down a^*.

molecules of (30) exhibit no close intermolecular contacts. The distance between two neighbouring S atoms (*i.e.*, between the reference molecule at x, y, z and the molecule at $-x$, $-y$, $1 - z$) is 4.36(2) Å, which exceeds significantly the sum of their van der Waals radii. This loose packing is reflected in the large average volume occupied by a non-hydrogen atom (18.9 Å^3, D_c = 1.25 g cm^{-3}) compared with (4) (17.9 Å^3, D_c = 1.33 g cm^{-3})[34] or 3-carboxymethylthio-1,5-diphenylformazan (16.8 Å^3, D_c = 1.42 g cm^{-3}).[96] The looser packing in (30) can be ascribed to the fact that the *S*-methyl group projects above the mean plane of the molecule in (30), whereas in the latter two compounds the groups attached to sulphur lie virtually in the plane of the molecule.

Hydrogen bonding

The imino proton H(11) is internally hydrogen-bonded to S(18), effectively locking the molecule in the *anti* configuration. The H(11)···S(18) distance of 2.42(5) Å [for a fixed N(11)-H(11) length of 1.00(1) Å] is significantly less than the sum of the van der Waals radii,[126] while the N(11)···S(18) separation is 2.94(1) Å. The H(11)···S(18) distance is the same as that found in xanthane hydride,[175] where the H atoms were located approximately and the presence of an almost linear intermolecular N-H···S hydrogen bond was reported, and is the same as the intramolecular H···S distance in *S*-isopropyldithizone,[92] which has the same configuration of the N-N-C-N-N chain as (30). Although the distances are favourable for a strong intramolecular hydrogen bond, the stereochemistry of the molecule does not allow linearity of the N(11)-H(11)···S(18) angle [97(4)°] and thus the hydrogen bond formed is considerably weakened. Hydrogen bonding is nevertheless favoured here by the fact that in the configuration adopted one of the lone pairs of electrons on S(18) is orientated towards H(11). Consideration of the angles around N(11)

(Table 28) indicates a small attraction of H(11) towards S(18). Very similar distances have been found in this work (Chapter V) for the intramolecular N-H···S hydrogen bonds in phenylmercury(II) dithizonate (35) and methylmercury(II) dithizonate (36). The H···S distances are 2.43(8) (35) and 2.40(9) Å (36) [for constrained N-H lengths of 1.00 (1) Å] while the N···S separations are 2.86(2) (35) and 2.92(3) Å (36).



(35) : R = phenyl

(36) : R = methyl

The stretching frequency ν(N-H) in (30) is at 3270 cm^{-1} (KBr disk) and in (35) and (36) is at 3253 and 3255 cm^{-1} respectively, while the *syn*-configuration compounds (4), (29) and 3-carboxymethylthio-1,5-diphenylformazan,[96] in which intramolecular N-H···N hydrogen bonds exist [as (4d)] show ν(N-H) at 3338, 3341, and 3332 cm^{-1} respectively. The substantial difference of 68 cm^{-1} between ν(N-H) in (4d) and (30f) leads to the conclusion that there is a special stability associated with the intramolecular N-H···S hydrogen bond in (30) [and, for that matter, in (35) and (36)]. In terms of distances, the strength of hydrogen

bonding may be regarded[112] as directly related to the difference $[r(H) + r(B)] - d(H\cdots B)$ where $r(H)$ and $r(B)$ are the van der Waals radii for the H atom and the acceptor atom B, respectively. This overlap is 0.55 Å in (30f) and 0.56 Å for (4d) [where H(11)···N(8) is 2.21 Å and N(11)···N(8) is 2.62 Å] and does not explain the apparently stronger hydrogen bond found in (30). Flett[176] has pointed out an anomalously large shift of ν(N-H) to lower wavenumber found for intermolecular N-H···S hydrogen-bonding thioamides.

There is in the *anti* structure (30f) a noticeable shortening of the N(10)-N(11) formal single bond [1.326(6) Å] over the corresponding lengths found in the *syn* structures (4d) [1.344(4) Å] and 3-carboxymethylthio-1,5-diphenylformazan [1.352(6) Å]. Now the *p*-electrons on nitrogen in a conjugated C-N chain are delocalized if this atom is involved in three σ bonds (especially if one of these is to hydrogen). As a result the sum of the bond orders of that N is well above 3, *viz* between 3.4 and 3.7.[121] If the sum of the bond orders around N(11) is therefore assumed to be 3.6, and using bond-length *versus* bond-order curves for C-N and N-N bonds in which both atoms are assumed to have sp^2 hybridization,[121] bond orders of 1.02 and 1.06 may be derived for the N-H bonds in (4) and 3-carboxymethylthio-1,5-diphenylformazan respectively. The N-H bond orders in (30), (35), (36), and *S*-isopropyldithizone are found to lie in the range 0.92 - 0.95 and thus the lower ν(N-H) found in (30) and related structures may, in part at least, be a result of increased electron delocalization over the thiocarbazone chain in *anti* configurations [in which N(10)-N(11) has more double-bond character than in *syn* configurations] rather than of a significantly stronger hydrogen bond to sulphur. The relatively small differences in N-H bond orders, however, may make this argument somewhat tenuous, although the differences are real if the e.s.d.'s

of the bond lengths are not too optimistic.

Conclusion

Why this *anti*,s-*trans* configuration (30f) should be preferred to the *syn*,s-*trans* configuration [as in *S*-methyldithizone (4d)] is not obvious. That the same extended-chain *anti* configuration is found in *S*-isopropyldithizone[92] indicates that the adopted configuration is not predominantly a result of steric effects due to the *ortho*-substituted aryl groups in (30). Indeed, there seems to be no reason why the *o*-tolyl methyl groups or an *S*-isopropyl group should have any effect on the configuration adopted in the structures *per se*. The observed configuration of the isopropyl derivative may be stabilized by a slightly stronger N-H···S hydrogen bond resulting from increased localization of electron density induced on the sulphur atom by the isopropyl group, although isopropyl groups are not significantly more electron-releasing than methyl groups. (Taft's[177] polar substituent constants σ^* for Me and Pr^i groups are 0.00 and -0.19, respectively.) Apparently molecular-packing considerations in the crystal are of prime importance in determining the configuration adopted by these molecules in the solid state.

3. Spectroscopic studies

At this point the solid state structure of the yellow *o*-tolyl compound (30f) is known (*anti*,s-*trans*). On dissolving in chloroform these crystals give initially a yellow solution (λ_{max} 420 nm) which after several days in the dark turns brownish to form an equilibrium mixture with a pink isomer having a peak at 560 nm. The solid state structure of the red *p*-tolyl compound (29d) is known to be the same as the parent *S*-methyldithizone (4d) (*syn*,s-*trans*). On dissolving in chloroform these crystals give initially a pink solution (λ_{max} 550 nm) which slowly turns brownish to form an equilibrium mixture with a yellow isomer having a peak at *ca*. 420 nm. Presumably the pink isomers of (4), (29), and (30) are isostructural, as are all the yellow isomers of the compounds.

This was demonstrated by ^{1}H n.m.r. spectroscopy, where in addition to (4), (29), and (30) the corresponding -SCD_3 analogues were examined in order to facilitate unambiguous assignment of the methyl resonances (Table 29). The results obtained from both chloroform and benzene solutions afforded the same conclusions, the benzene solution spectra showing better separation of the methyl resonances. In a freshly prepared (pink) solution of (29) the *p*-tolyl methyl groups give rise to a single resonance integrating for 6H. Their equivalence is consistent with the closed ring *syn*,s-*cis* structure (29a). However, the *syn*,s-*trans* (29d) configuration [already shown to occur in crystals of (4)[34]] is also possible if the equivalence of the two methyl groups is achieved by interconversion, fast on the n.m.r. time scale, between equivalent tautomers of (29d) involving rotation about the C-N single bond, with the mesomeric *syn*,s-*cis* structure (29a) as intermediate. However, it appears

TABLE 29 : ^{1}H CHEMICAL SHIFT VALUES[a] FOR IMINO AND METHYL RESONANCES OF *S*-METHYLDITHIZONE (4) AND ITS *p*-TOLYL (29) AND *o*-TOLYL (30) HOMOLOGUES IN $CDCl_3$ AND, IN PARENTHESES, C_6D_6

		Fresh solution		Equilibrium mixture after 70 h	
Compound (4)	-N*H*	10.26	(10.02)	10.26	(10.02)
				9.46	(9.24)
	$^1J(^{15}N\text{-}H)$/Hz	47.6	(46.9)	47.6	(46.9)
				92.2	(93.0)
	-SC*H*$_3$	2.54[b]	(2.29[b])	2.54[b]	(2.29[b])
				2.40[b]	(1.92[b])
Compound (29)	-N*H*	10.22	(10.06)	10.19	(10.06)
				9.43	(9.26)
	-SC*H*$_3$	2.52[b]	(2.32[b])	2.52[b]	(2.32[b])
				2.39[b,c]	(1.95[b])
	ArC*H*$_3$	2.39	(2.09)	2.39	(2.09)
				2.42	(2.09[c])
				2.34	(2.03)
Compound (30)	-N*H*	9.53	(9.41)	9.52	(9.41)
				10.28	(10.21)
	-SC*H*$_3$	2.43[b]	(1.95[b])	2.43[b]	(1.95[b])
				2.51[b]	(2.35[b])
	ArC*H*$_3$	2.40	(1.98)	2.40	(1.98)
		2.72	(2.69)	2.72	(2.69)
				2.53	(2.29)

[a] 100 MHz ^{1}H n.m.r. spectra at ambient temperature. Chemical shifts (δ, ppm) are relative to TMS. All -N*H* peaks disappear on addition of D_2O.

[b] Resonance disappears in spectrum of -SCD_3 analogue.

[c] Apparent from peak integration.

that upon dissolving in chloroform the solid state *syn*,s-*trans* structure (29d) immediately becomes *syn*,s-*cis* (29a) by rotation about the C-N single bond to give the mesomeric closed-ring system (29c). [The alphabetic designation of isomers corresponds to that used for the general formazan (2) in Chapter II.] This is founded on the fact that when N(1) and N(5) in *S*-methyldithizone (4) are labelled with ^{15}N (spin quantum number = $\frac{1}{2}$) the imino proton resonance at δ 10.26 becomes a triplet (1:2:1) with an apparent coupling constant of 47.6 Hz. There was no change in the spectrum when run at -40°C. The triplet means that the proton is coupling to two ^{15}N nuclei, which, when the coupling constant of virtually half the usual ^{15}N-H coupling value is taken into account,[155] provides evidence for either a very rapid intramolecular exchange of the proton between N(1) and N(5) consistent with the rapid tautomeric equilibrium (4a) $\rightleftharpoons$ (4b),[156] or a mesomeric structure (4c) in which the hydrogen atom is formally situated at an equal distance from N(1) and N(5) with a consequent increase in N-H distance and decrease in ^{15}N-H coupling.[157,158] In either case the configuration is *syn*,s-*cis*, and the same structure was found in the red 3-nitro-1,5-diarylformazans (Chapter II). The more deshielded imino proton (δ 14.4 - 15.4) and unobserved ν(N-H) in the nitroformazans probably results from the presence of the strongly electron-withdrawing nitro-group compared with the SCH_3 group in these compounds. The two methyl groups in 2,3-di(*p*-tolyl)-2*H*-tetrazolium-5-thiolate [(32); Ar = *p*-tolyl; the *p*-tolyl homologue of 'dehydrodithizone'], which is locked in the closed-ring configuration, give a single peak at δ 2.43 in $CDCl_3$, which may be compared with the δ 2.39 singlet in a fresh $CDCl_3$ solution of (29).

As the solution of (29) gradually changes colour from pink to brown, two new *p*-tolyl methyl resonances slowly develop until after 3 days in the dark three *p*-tolyl methyl lines are found (Table 29), still integrating *in toto* for 6H. The new resonances are attributed to the magnetically non-equivalent *p*-tolyl methyl groups of isomer (29f) produced by a *syn* $\longrightarrow$ *anti* isomerization about the formal -C=N- double bond. This would result in two rotamers (29e) $\rightleftharpoons$ (29f) but structure (29e) is less favoured due to repulsion of the lone pairs on N(1) and N(4). The spectrum of a $CDCl_3$ solution of the ^{15}N-labelled *S*-methyldithizone (4) after 3 days in the dark shows the imino proton resonance shifted upfield to δ 9.46 where it now appears as a doublet with ^{15}N-H coupling constant of 92.2 Hz. This doublet, which shows the proton coupling to only one ^{15}N atom, is superimposed upon the triplet of the fresh solution. The $^1J(^{15}N\text{-H})$ value is normal[155] and provides conclusive evidence for the single *anti*,s-*trans* configuration as the yellow isomer, with the possibility of a contribution from the less-favoured s-*cis* rotamer. Once again the spectrum at -40°C was identical with that at ambient temperature.

The proton spectrum of a fresh solution in $CDCl_3$ of the ^{15}N-labelled *S*-methyldithizone and of the equilibrium mixture of pink and yellow isomers is shown in Figure 18. An interesting feature of the imino proton triplet in the fresh solution is the very low intensity superimposed doublet (J = 47.6 Hz) centred at the same chemical shift as the triplet. This arises because the compound was labelled with 96 atom-% ^{15}N and the presence of 4 atom-% ^{14}N gives rise to a very low intensity doublet corresponding to the situation where only one terminal nitrogen [N(1) or N(5)] is labelled with ^{15}N.

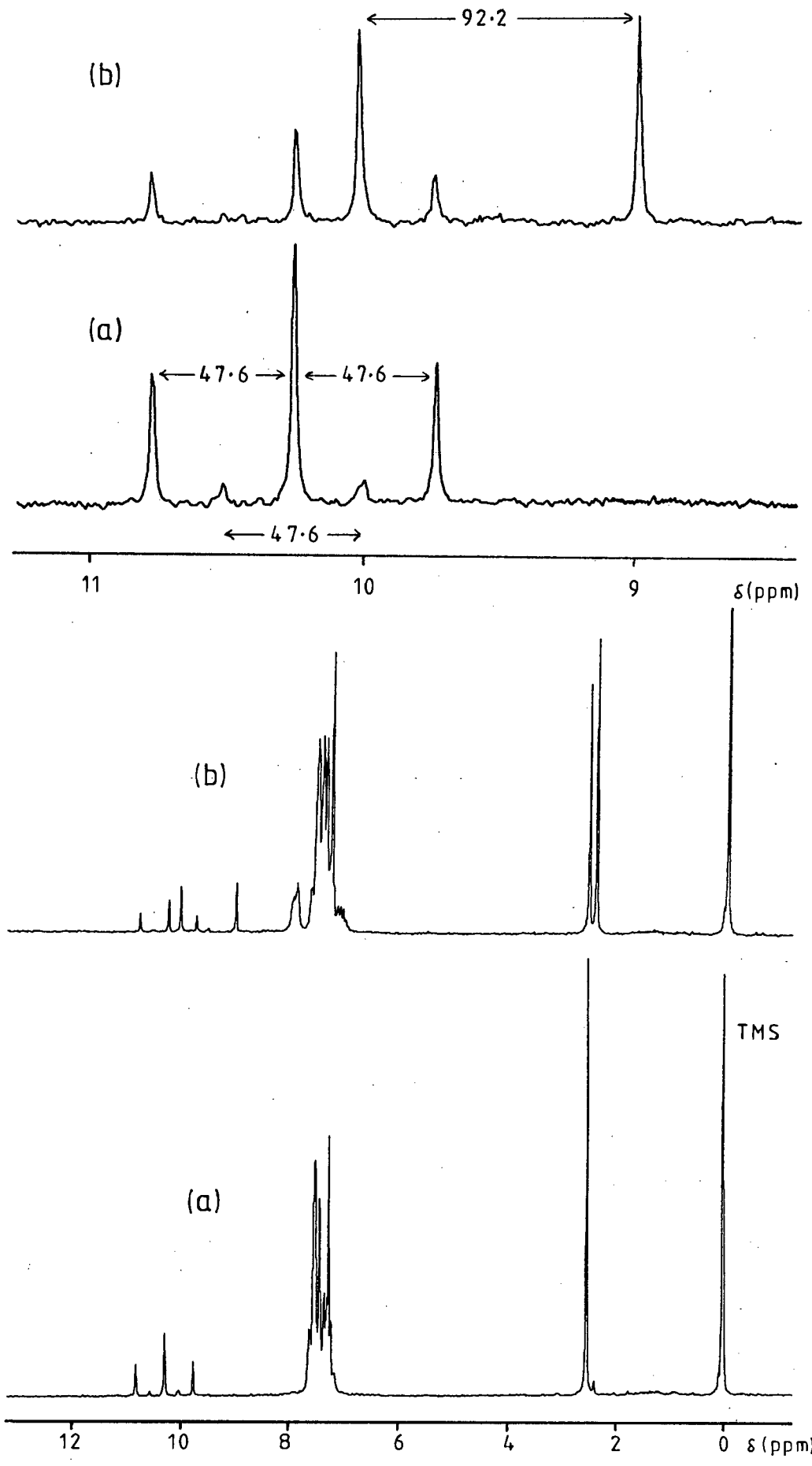


FIGURE 18 : ^{1}H n.m.r. spectrum of *S*-methyldithizone (4) labelled at N(1) and N(5) with 96 atom-% ^{15}N as (a) fresh (pink) solution in $CDCl_3$ and (b) equilibrium mixture of pink and yellow isomers after 70 h. Above: The N*H* region with $^{1}J(^{15}N\text{-}H)$ in Hz.

This shows that for 4% of the time (or in 4% of the molecules) the proton is coupled to only one nitrogen atom, and the coupling constant, halved when compared with usual values,[155] may be interpreted as before in terms of either rapid intramolecular proton exchange or mesomerism in the *syn*,s-*cis* configuration.

The magnetically non-equivalent *o*-tolyl methyl groups in a fresh (yellow) solution of (30) show two resonances of equal intensity (Table 29) derived from form (30f), as expected from the *X*-ray analysis of the yellow crystals of (30). On standing in the dark, isomerization about the C=N double bond and rotation about the C-N single bond yields the pink *syn*,s-*cis* closed-ring configuration [(a) $\rightleftharpoons$ (b), or (c)] which gives rise to an additional *o*-tolyl methyl resonance (δ2.53) in the spectrum of the equilibrium mixture. The *o*-tolyl homologue of 'dehydrodithizone' [(32); Ar = *o*-tolyl], which is locked in the closed-ring configuration, shows a single line at δ 2.30 for the two methyl groups.

For both compounds (29) and (30) the resonances of the methyl and imino groups derived from each of the isomers are of approximately equal intensity, indicating that the two forms of (29) and (30) co-exist at equilibrium in roughly equal proportions in chloroform and benzene solutions. A new *S*-methyl resonance is observed in the equilibrium mixture given by (29) which occurs at virtually the same chemical shift value as that given by a fresh solution of (30), and similarly *mutatis mutandis* for the equilibrium mixture given by (30) (Table 29). Clearly isomerization occurs in chloroform and benzene solutions of both (29) and (30) resulting in equilibrium mixtures of configurations (a) $\rightleftharpoons$ (b) [or the mesomeric (c)] and (f). The homologues (29) and (30) give

very similar ^{1}H n.m.r. spectra with one obvious difference, *viz* the chemical shifts of the tolyl methyl groups: in (30) the relatively large difference in chemical shift values of the two *o*-tolyl methyl resonances in, *e.g.*, C_6D_6 [(30f) 0.71 ppm] over the *p*-tolyl methyl lines of the same configuration [(29f) 0.06 ppm] is attributable to the magnetic anisotropy effect of the azo-group to which one of the methyl groups is subjected in structure (30f).

The broad-band ^{1}H-decoupled ^{13}C n.m.r. spectrum of *S*-methyldithizone (4) labelled at C(3) with 91 atom-% ^{13}C (Figure 19) shows a peak at 146.3 ppm downfield from TMS which diminishes in intensity as a new peak grows at 147.4 ppm due to the formation of the yellow isomer. These chemical shifts compare well with the kind of carbon atom in the 3-position of 1,2,-4-triazole [(28), Chapter II] (148.1 ppm)[161] and are typical of :C=N- in heteroaromatics. Some of the (unenriched) ^{13}C resonances of the phenyl groups are also observed as low intensity peaks. The spectrum of a solution which has reached equilibrium is shown in Figure 19 (inset), as well as the ^{1}H-coupled spectrum obtained by gated proton irradiation of the equilibrium solution. Each C(3) peak is split into what appear to be triplets. They cannot be real triplets, however, because that would mean that the ^{13}C resonance in each case was being split by two protons; the molecular formula shows that ^{13}C at C(3) may couple through three bonds with either the $-SCH_3$ protons or the NH proton or with both of these groups. That coupling with both of these groups occurs is suggested by the asymmetry of the 'triplets' (splitting 2.9 and 4.4 Hz in either case) which are probably unresolved superimpositions of a quartet (from $-SCH_3$) and a doublet (from NH). Coupling of ^{13}C(3) to both groups was unambiguously confirmed when

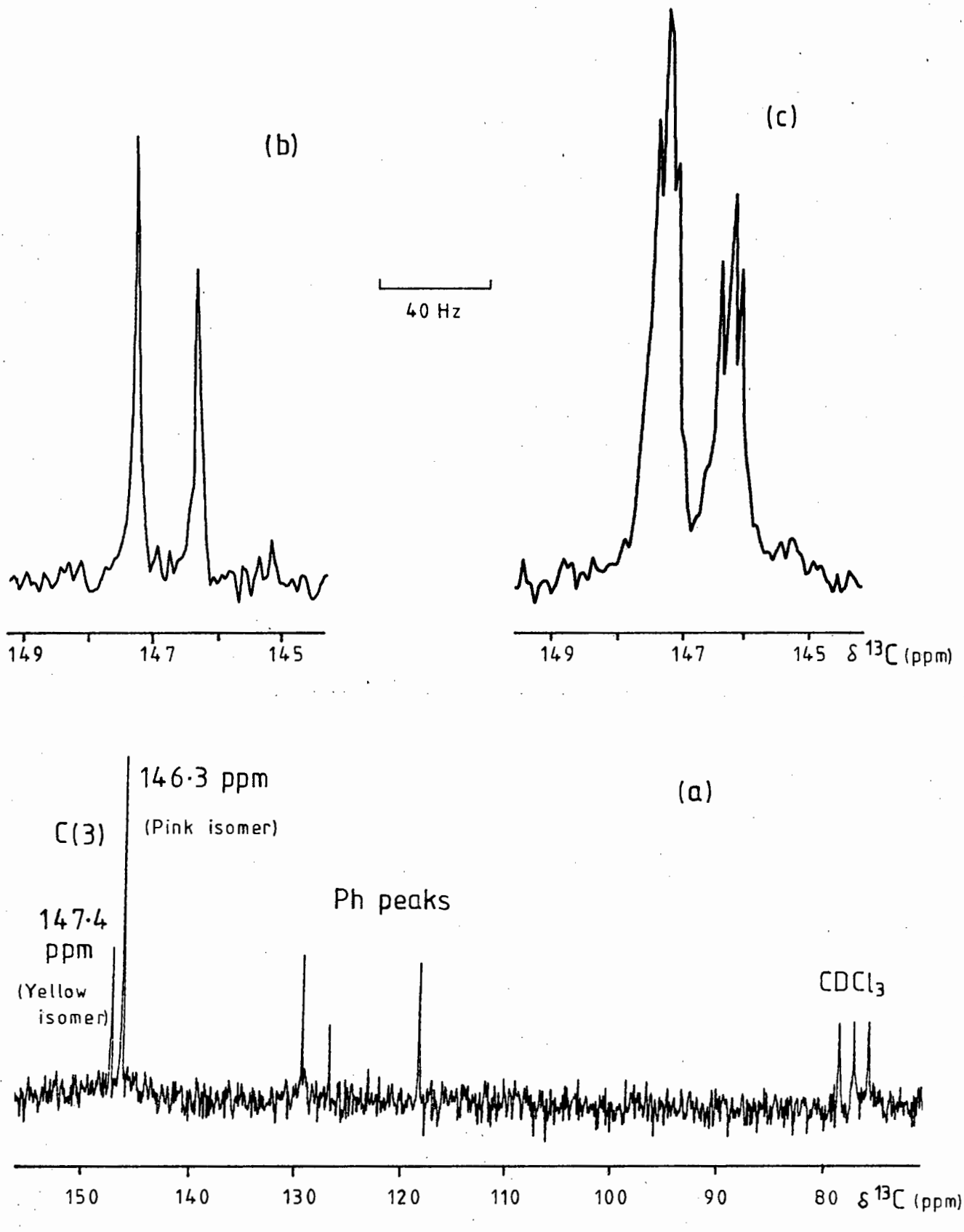


FIGURE 19 : ^{13}C n.m.r. spectrum of *S*-methyldithizone (4) labelled at C(3) with 91 atom-% ^{13}C. Chemical shifts are downfield from external TMS. (a) ^{1}H-decoupled spectrum of $CDCl_3$ solution of (4) after 2 h; (b) peaks due to C(3) at equilibrium after 70 h; (c) ^{1}H-coupled spectrum of peaks due to C(3) after 70 h.

the ^{1}H n.m.r. spectrum of the ^{13}C-labelled *S*-methyldithizone was measured (Figure 20). This shows the two -SC*H*$_3$ peaks arising from the two isomers as doublets [*i.e.*, split by $^{13}C(3)$] with the same three-bond coupling constant $J(^{13}C\text{-}S\text{-}C\text{-}H)$ of 3.7 Hz. Both N*H* peaks also appear as doublets [*i.e.*, split by $^{13}C(3)$] but with different coupling values. The $J(^{13}C\text{-}N\text{-}N\text{-}H)$ value for the pink isomer is 2.9 Hz while that for the yellow isomer is 4.4 Hz. These values differ because the coupling is transmitted through bonds which are directly involved in the isomerization, whereas the $J(^{13}C\text{-}S\text{-}C\text{-}H)$ values are identical since the -SCH_3 part of the molecule is virtually unaffected by the isomerization. The precise influence of the nature of the bonding network giving rise to three-bond C-H couplings through heteroatoms is not clear-cut.[162]

The approach to an equilibrium mixture starting from either the pink isomer [(4) and (29)] or the yellow isomer (30) can also be followed clearly by observation of the ν(N-H) stretching frequency: the intramolecular N-H···N and N-H···S hydrogen bonds differ significantly in strength and show a separation in ν(N-H) of *ca.* 90 cm^{-1} (Table 30, Figure 21). The change in the position of the imino proton resonance (Table 29) also reflects this difference in internal hydrogen bonding. It is surprising that the ν(N-H) frequencies of the solids (4) and (29) (Table 30) do not change significantly upon dissolving the solids in CCl_4. If immediate rotation about the C-N single bond occurs on dissolving the solid to yield the *syn*,s-*cis* [(a) $\rightleftharpoons$ (b), or (c)] isomer from the solid state *syn*,s-*trans* (d) structure [as was convincingly shown by the ^{1}H n.m.r. spectrum of the ^{15}N-labelled analogue of (4)], one would expect a significant difference between ν(N-H) in the solid state and in solution.

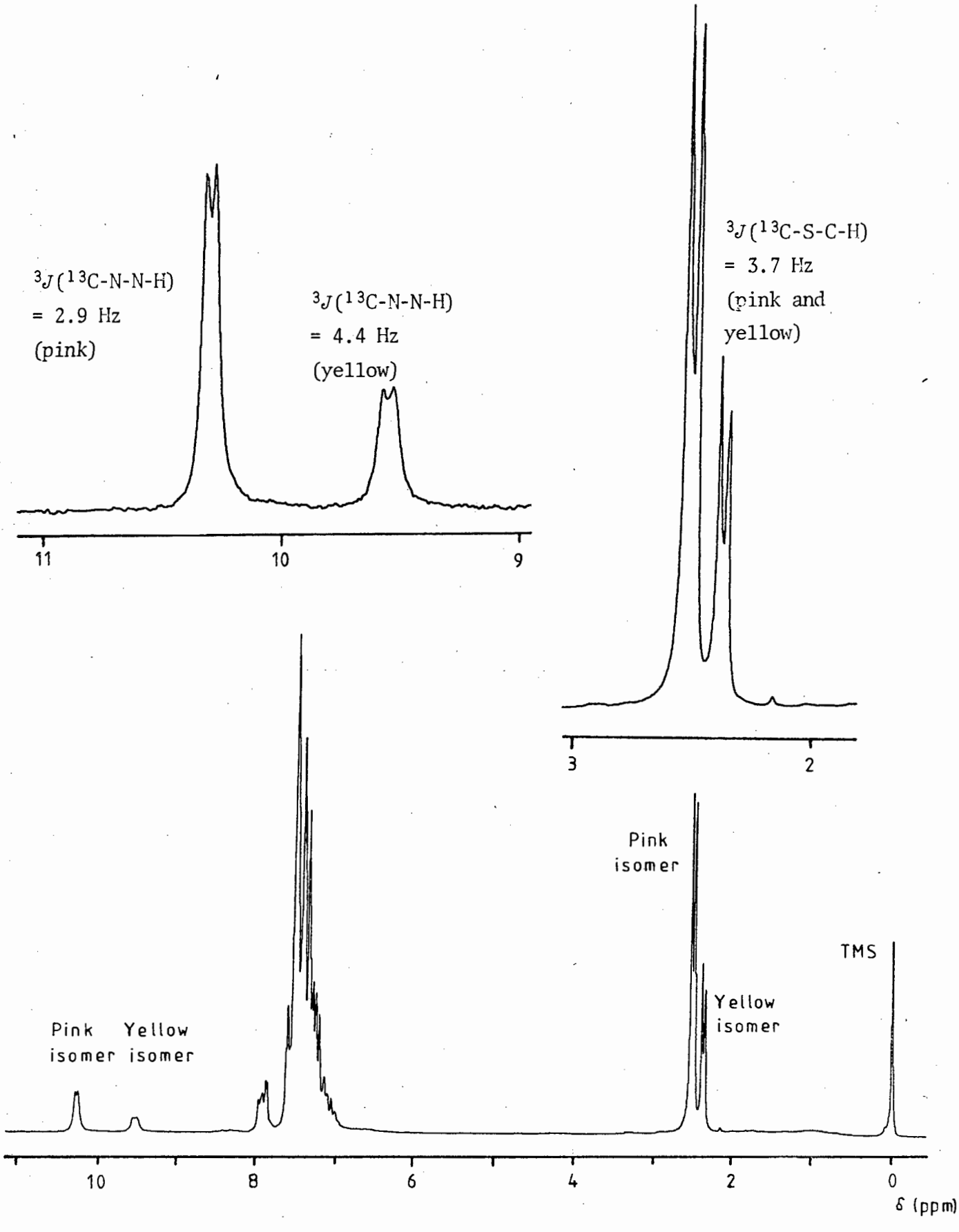
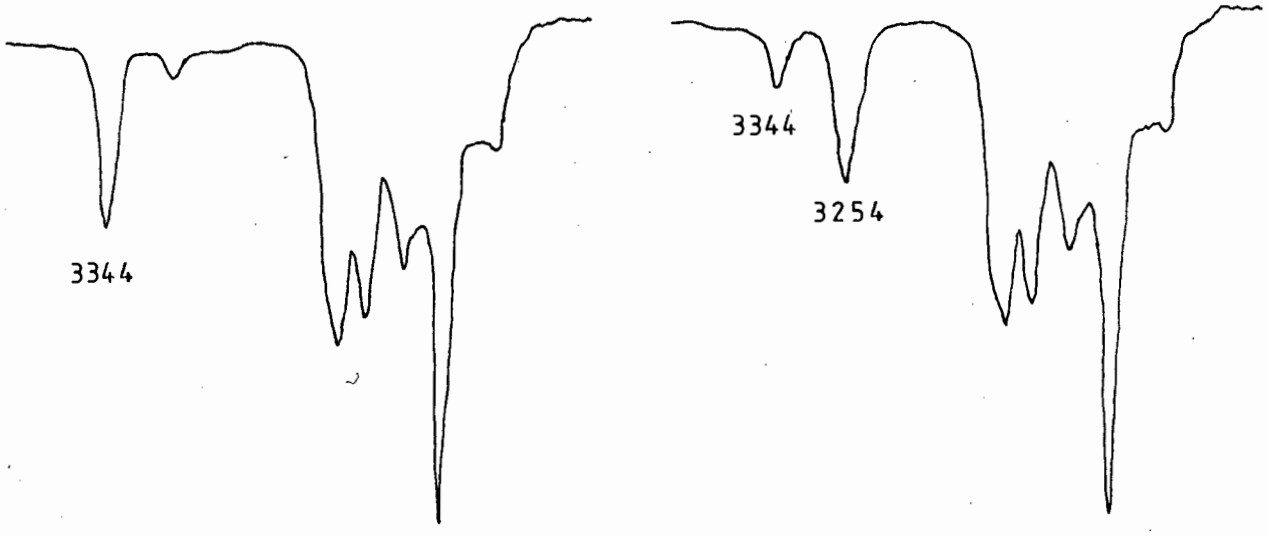


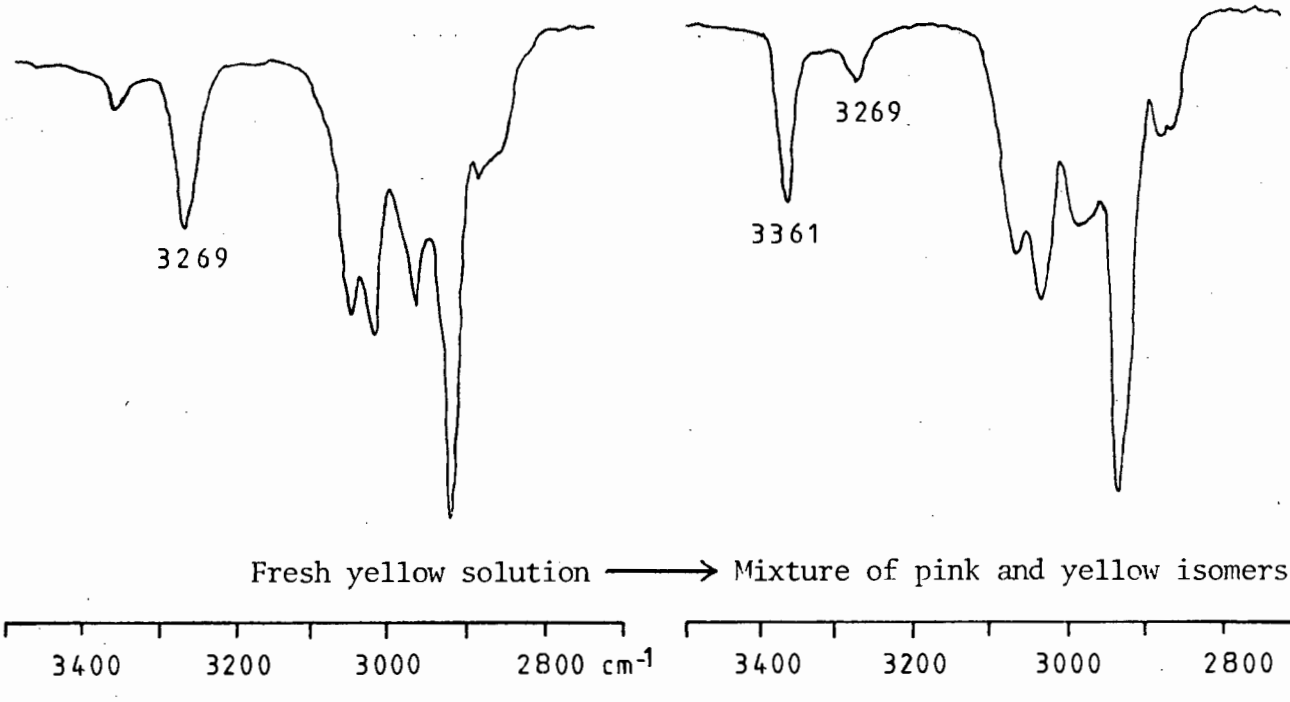
FIGURE 20 : ^1H n.m.r. spectrum of a $CDCl_3$ solution of *S*-methyldithizone (4) labelled at C(3) with 91 atom-% ^{13}C 2 hours after preparation. Coupling of the SCH_3 and NH protons to $^{13}C(3)$ (enlargements shown above) is observed in peaks derived from both the pink and yellow isomers.

3-Methylthio-1,5-di(*p*-tolyl)formazan (29)



Fresh pink solution ⟶ Mixture of pink and yellow isomers

3-Methylthio-1,5-di(*o*-tolyl)formazan (30)



Fresh yellow solution ⟶ Mixture of pink and yellow isomers

FIGURE 21 : I.r. spectra of fresh solutions in CCl_4 (left hand side) of (29) (upper) and (30) (lower) and equilibrium mixtures of pink and yellow isomers after 70 h (right hand side). The changes in the ν(N-H) bands are the only significant changes in the spectra consequent upon isomerization. It can be seen that isomerization has already started in the 'fresh' solutions (left hand side).

TABLE 30 : ν(N-H)/cm^{-1} FOR *S*-METHYLDITHIZONE (4) AND ITS *p*-TOLYL (29) AND *o*-TOLYL (30) HOMOLOGUES

Compound	Solid[a]	Fresh solution[b]	Equilibrium mixture after 70 h
(4)	3338	3342	3342 3253
(29)	3341	3344	3344 3254
(30)	3270	3269	3269 3361

[a] As KBr pressed disks. [b] In CCl_4.

However, other workers[77] have recently pointed out that the *syn*,s-*cis* [(a) $\rightleftharpoons$ (b), or (c)] isomer cannot be distinguished from the *syn*,s-*trans* (d) structure on the basis of ν(N-H) alone, and this curious discrepancy remains unexplained.

Several authors have speculated on the nature of the pink and yellow isomers of 3-methylthio-1,5-diphenylformazan [(4); *S*-methyldithizone][28,69,70,166-169] and, as indicated in Chapter II, of formazans in general.[8,30-33,74-76,80-83] The results of the present work explain the isomerism occurring in solutions of *S*-methyldithizone and may be applied to that found in many other formazans. It has been shown that the red (longer wavelength) formazans are in the closed *syn*,s-*cis* configuration, which

may involve very rapid intramolecular proton transfer [(2a) $\rightleftharpoons$ (2b)] or a single mesomeric structure (2c); in the limit these may be indistinguishable, but are certainly not 'quasi-aromatic' or 'non-classical aromatic' (2*l*). The yellow (shorter wavelength) isomer clearly has the open *anti*,s-*trans* structure (2f), but in both cases rotamers may be possible. It should be stressed that the results hold only for the symmetrically substituted formazans [(2); $R^1 = R^2$] in the solvents studied. These assignments are opposite to those proposed by *e.g.*, Burns and Duncan[69] or Carlin,[70] but they support the speculative configurations proposed by Kuhn and Weitz in 1953.[31]

4. Experimental

General and spectroscopic

Visible absorption, diffuse reflectance, i.r., and n.m.r. spectra were generally measured on the same instruments and under the same conditions as the work reported in Chapter II. Special care was taken in cleaning the optical cells, the n.m.r. tubes, and the glassware in which solutions of the methylated derivatives of dithizone were handled so as to prevent catalytic isomerization. The cleaning was done by soaking the apparatus in a chromic acid bath, washing with hot water, and then soaking in a strong ammoniacal solution of the disodium salt of EDTA. Finally the apparatus was thoroughly rinsed with deionized water and dried in an oven at 130°C. New and unused NaCl plates were fitted to the i.r. solution cells for this study, and a 0.5 mm path length was used.

Proton n.m.r. spectra were recorded on the Varian XL-100 CW spectrometer, while ^{13}C n.m.r. spectra were obtained on the Bruker WH-90DS spectrometer under similar conditions as used for the work reported in Chapter II. Typically a 30° pulse with a 1 second delay was used (acquisition time 682 milliseconds). Satisfactory spectra were obtained from about 3000 transients. The use of shiftless relaxation agents to shorten the necessary delay between pulses was prohibited by their catalytic effect on the isomerization being monitored. For the same reason shifts were taken relative to the central line of the $CDCl_3$ ^{13}C signal rather than using internal TMS. Shifts relative to TMS were obtained from the relation[161] $\delta(TMS) = \delta(CDCl_3) + 76.9$ and are accurate to an estimated

0.1 ppm. Proton coupled spectra were made in the gated proton irradiation mode[163] using 1.0 W power centred at 3.3 kHz.

Preparations

General preparative procedures and facilities were unchanged from the work reported in Chapter II.

3-Methylthio-1,5-diphenylformazan [*S*-methyldithizone; (4)]

A solution of Merck analytical reagent grade dithizone [(1); 5.0 g] in dilute aqueous alkali (15 cm^3 of 2 *M* NaOH solution and 50 cm^3 of water) was shaken well with dimethylsulphate (2.6 g, 1.9 cm^3) in a glass-stoppered flask. The initial orange colour of the solution rapidly disappeared and a black solid separated almost immediately. A further portion of sodium hydroxide solution (15 cm^3 of 2 *M*) was added, and the mixture was heated gently on a water-bath for 30 minutes to destroy any excess of dimethylsulphate. On cooling, the mixture was extracted with successive quantities of chloroform and the combined organic extract was washed several times with dilute aqueous ammonia solution to remove unmethylated dithizone, and then with water and finally the organic extract was dried over sodium sulphate. Removal of the solvent left impure (4) which was purified by chromatography on neutral alumina. Carbon tetrachloride was found to be a suitable solvent for introduction of the material on the top of the column, and elution was performed with benzene. The main band which developed was dark brown in colour; it was preceded by a faint pink band and followed by one of a lighter brown. While the main band was moving off the column the eluent was collected;

subsequent removal of the solvent gave the desired solid product (4). Recrystallization from ethanol gave sharp black needles with a bronze reflex [2.85 g, 54.0%; m.p. 118-120°C decomp. (lit.[28] 119-120)]. (Found: C, 62.3; H, 5.35; N, 20.8%. Calc. for $C_{14}H_{14}N_4S$: C, 62.2; H, 5.2; N, 20.7%.)

3-Methylthio-1,5-di(*p*-tolyl)formazan (29)

This was prepared in the same way as (4) above by methylation of 1.0 g of the *p*-tolyl homologue of dithizone, the preparation of which is reported in Chapter IV. The crude product obtained was purified by column chromatography and recrystallized twice from ethanol to yield sharp black needles of the *p*-tolyl homologue of *S*-methyldithizone (29) (0.47 g, 45.0%; m.p. 128-130°C decomp.). (Found: C, 64.5; H, 6.2; N, 18.7%. $C_{16}H_{18}N_4S$ requires C, 64.4; H, 6.1; N, 18.8%.)

3-Methylthio-1,5-di(*o*-tolyl)formazan (30)

This compound was prepared in the same way as (4) above by methylation of 1.0 g of the *o*-tolyl homologue of dithizone, the preparation of which is reported in Chapter IV. The crude product was purified by column chromatography and recrystallized twice from ethanol to give yellow-orange plates of (30) (0.52 g, 49.8%; m.p. 130-133° decomp.). (Found: C, 64.3; H, 6.0; N, 18.7%. $C_{16}H_{18}N_4S$ requires C, 64.4; H, 6.1; N, 18.8%.)

2,3-diphenyl-2*H*-tetrazolium-5-thiolate ['dehydrodithizone'; (32), Ar = Ph]

A solution of dithizone (1.0 g) in chloroform (300 cm^3) was stirred mechanically for 2 hours with a solution of potassium hexacyanoferrate(III) (3.2 g) and potassium carbonate (3.0 g) in distilled water (100 cm^3). The organic layer was removed, dried with sodium sulphate, and the solvent allowed to evaporate at room temperature. The residue was taken up in boiling ethanol, treated with animal charcoal, filtered, and allowed to

cool overnight to yield orange-red crystals of [(32), Ar = Ph] which were dried *in vacuo* over silica gel [0.65 g, 65%; m.p. 173° decomp. (lit.[5] 173° decomp.)]. (Found: C, 61.2; H, 4.0; N, 21.85%. Calc. for $C_{13}H_{10}N_4S$: C, 61.4; H, 4.0; N, 22.0%.) The absorption spectrum in chloroform showed a strong band at 267 nm and a weaker band at 470 nm.

The *p*-tolyl and *o*-tolyl homologues [(32), Ar = *p*-tolyl or *o*-tolyl] were prepared in 34% and 29% yields, respectively, by exactly the same method, starting from the corresponding substituted dithizones. The synthesis of these substituted dithizones is reported in Chapter IV. The ^{13}C- and ^{15}N-labelled analogues were also prepared in this way, again from the corresponding labelled dithizones (Chapter IV), in 67% and 63% yields, respectively. These intermediates were all recrystallized but not analyzed before continuing with the following stage.

5-Deuteromethylthio-2,3-diphenyltetrazolium iodide [(33), Ar = Ph]

A solution of the mesoionic compound 'dehydrodithizone' [(32), Ar = Ph] from the above preparation (0.48 g) and trideuteromethyl iodide (CD_3I, 0.23 g) in chloroform (30 cm) was gently boiled under reflux for 1 hour during which time the colour of the solution changed from orange-red to dark brown. The solution was treated with animal charcoal and filtered; on cooling a precipitate formed which was yellow when isolated and washed with chloroform. Recrystallization from a boiling ethanol-diethyl ether mixture (3 : 1) gave yellow crystals of [(33), Ar = Ph] which were dried *in vacuo* over silica gel (0.67 g, 89.5%).

The *p*-tolyl and *o*-tolyl homologues [(33), Ar = *p*-tolyl or *o*-tolyl] were similarly prepared from the corresponding substituted dehydrodithizones in equally good yield, except that the *o*-tolyl homologue could not be

recrystallized; however, the oil was successfully used in the subsequent stage of the synthesis (see below). The ^{13}C- and ^{15}N-labelled analogues of the diphenyltetrazolium iodide were similarly prepared from the corresponding labelled dehydrodithizone using CH_3I in place of CD_3I.

3-Deuteromethylthio-1,5-diphenylformazan [(34), Ar = Ph]

A solution of the tetrazolium iodide [(33), Ar = Ph] from the above preparation (0.5 g), sodium hydroxide (0.25 g), and dextrose (2.0 g) in distilled water (100 cm^3) was warmed gently for a few minutes with vigorous stirring until a dark brown flocculent precipitate started to separate. On cooling in ice and acidification with dilute sulphuric acid the entire yield separated. This was collected, dried, and recrystallized from ethanol to give the $-SCD_3$ analogue of *S*-methyldithizone. Thin layer chromatography showed that the product needed no further purification (0.21 g, 62.1%).

The *p*-tolyl and *o*-tolyl homologues [(34), Ar = *p*-tolyl or *o*-tolyl] were similarly prepared from the corresponding substituted diaryltetrazolium iodides in similar yields. The di(*o*-tolyl)tetrazolium iodide [(33), Ar = *o*-tolyl], which was obtained as an oil (see above), was dissolved in ethanol and used in this synthesis successfully to give [(34), Ar = *o*-tolyl]. The ^{13}C- and ^{15}N-analogues of *S*-methyldithizone (4) were also prepared in this way from the corresponding labelled (but not deuterated) diphenyltetrazolium iodides synthesized above. This route to the ^{13}C- and ^{15}N-labelled analogues was chosen in preference to direct methylation of the corresponding labelled dithizones because it provided samples of the corresponding labelled dehydrodithizones and tetrazolium salts. These would be useful model compounds for comparing chemical shift values in ^{13}C and ^{15}N n.m.r. spectra with those of dithizone itself (see Chapter IV).

CHAPTER IV

THE STRUCTURE OF DITHIZONE IN SOLUTION

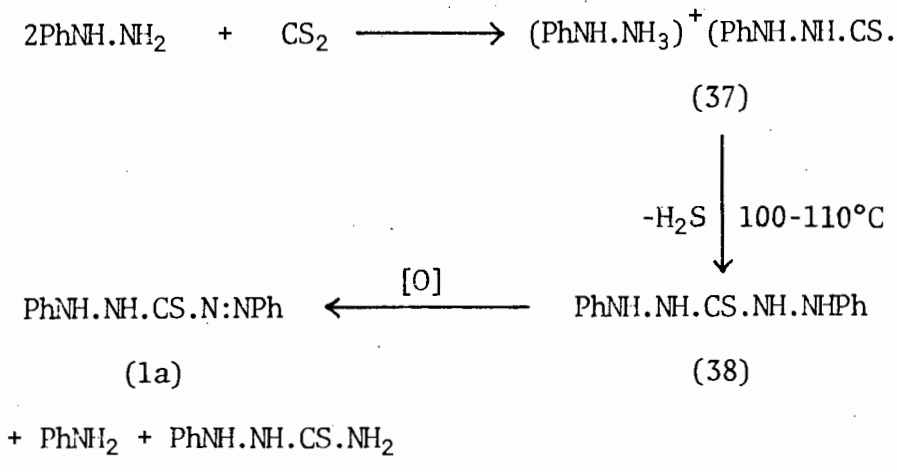
CHAPTER IV

THE STRUCTURE OF DITHIZONE IN SOLUTION

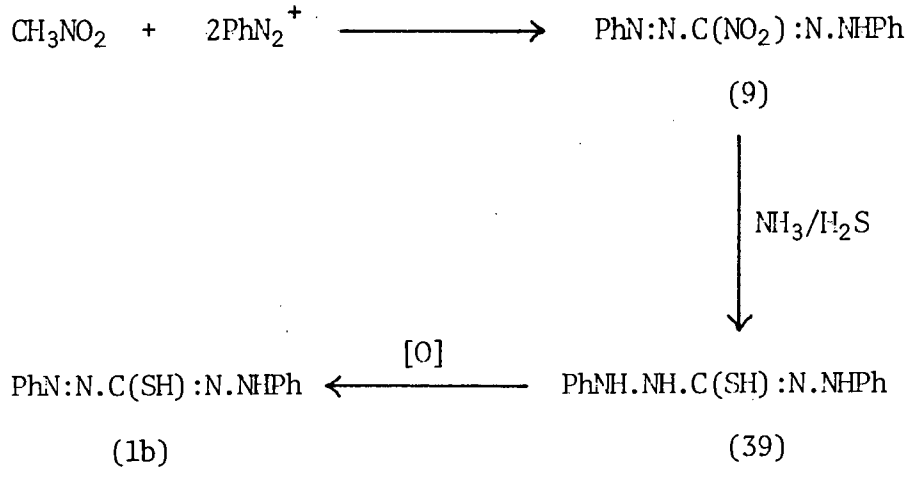
1. Introduction

The existence of thione-thiol tautomers in solution

During his extensive researches on derivatives of phenylhydrazine in 1878 Emil Fischer observed the formation of an unstable white salt (37) when solutions of carbon disulphide and phenylhydrazine in organic solvents were mixed. On careful heating, 'diphenylsulfocarbazid' (38) was obtained by loss of hydrogen sulphide, and oxidation ensued when this substance was warmed with dilute alkali.[1] In a later paper the almost black oxidation product ['diphenylsulfocarbazon', (1a)] was investigated in greater detail. Its empirical formula, $C_{13}H_{12}N_4S$, was confirmed and it was shown to form a compound $Zn(C_{13}H_{11}N_4S)_2 \cdot H_2O$ as beautiful red crystals resembling fuchsin. Water-insoluble 'salts' with silver (brown-violet) and mercury(I), with mercury(II) (brown-red), and with lead (red) were prepared but not analyzed: they were all readily soluble in chloroform.



Some years later Bamberger[178] described the preparation of the nitroformazan (9) by coupling nitromethane and benzenediazonium chloride, and in a paper of 1926, with Padova and Ormerod,[3] he showed that reduction with ammonium hydrosulphide gave 'dihydroformazylmercaptan' (39), which was recognised as being chemically identical with Fischer's 'diphenylsulfocarbazid' (38) and which was readily oxidized to 'formazylmercaptan' (1b), identical with the 'diphenylsulfocarbazon' (1a) which Emil Fischer had prepared nearly 50 years earlier.[1,2] This black product (m.p. 178°C) was found to give a 'salt' with both copper(II) and with lead, these salts analyzing correctly to $Cu(C_{13}H_{11}N_4S)_2$ and $Pb(C_{13}H_{11}N_4S)_2$ respectively; mercury(II) formed a red salt (m.p. ~220°C), which was not analyzed.

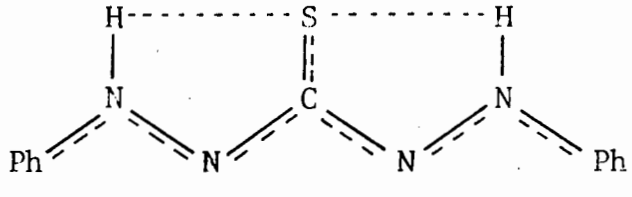


The formulation as a thioketone (1a) led to the name diphenylthiocarbazone (whence dithizone), whereas the formulation (1b) as a thiol is responsible for names in the formazan series such as 3-thio-1,5-diphenylformazan.

Fischer's synthesis of diphenylthiocarbazide, by pyrolysis of the salt (37), does not lead unambiguously to the structure (38), and both $PhNH.NH.CS.N(NH_2)Ph$ and $PhN(NH_2).CS.N(NH_2)Ph$ could be considered as alternatives,

with obvious implications as to the true structure of the oxidation product, dithizone. Corwin and Jackson[179] investigated these alternatives very thoroughly and concluded that the original formulation (38) was correct. Since dithizone dissolves readily in aqueous alkali and behaves as a typical thiol in forming insoluble compounds with mercury and other heavy metals, and in its ease of oxidation, the formulation (1b) would seem to be as reasonable as (1a), the structure favoured by Fischer's synthesis. Since the visual spectrum of solutions of dithizone in organic solvents shows two well defined bands at about 450 and 620 nm (Figure 1), it was assumed quite early that these correspond to the two tautomeric forms (1a) $\rightleftharpoons$ (1b) which coexist in solution, the thiol form (1b) being responsible for the band at shorter wavelength.[5]

When pure, dithizone ($C_{13}H_{12}N_4S$; M_r = 256.3) is a violet-black crystalline powder with a metallic reflex, of density 1.35 g cm^{-3} and m.p. 169°C (decomp.). X-Ray crystallography[10] has shown that the molecule (1c) is nearly planar, and of symmetry *mm* (C_{2v}) with the N-N-C-N-N chain extended and the C-S bond lying on the intersection of the mirror planes.



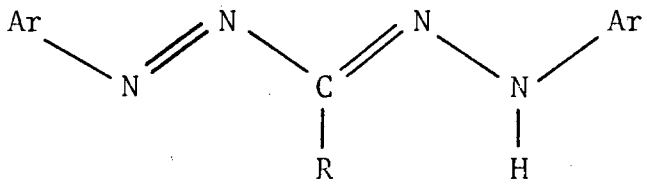
(1c)

The phenyl groups are twisted slightly out of the mean plane in opposite senses. It is evident from the measured bond lengths that π-electrons in the N-N-C-N-N chain are delocalized throughout and that there are no localized single or double bonds. The two imino hydrogen atoms are located as shown in (1c); both are hydrogen-bonded to the sulphur atom.

The diffuse reflectance spectrum of the solid shows a clearly defined band at 450 nm, similarly situated to the shorter wavelength band in CCl_4 or $CHCl_3$. Covering the region 580 - 610 nm is a broad shoulder which corresponds to the prominent peak at 620 nm in CCl_4 or 605 nm in $CHCl_3$. In solution the positions of $\lambda_{max,1}$ and $\lambda_{max,2}$ vary comparatively little with change of solvent, although there are striking changes in the relative magnitudes of the molar (decadic) absorption coefficients $\varepsilon_{max,1}$ and $\varepsilon_{max,2}$. The subscripts 1 and 2 are used to distinguish the longer and shorter wavelength, respectively. For example in chloroform $\lambda_{max,1}$ = 605 nm (ε = 4140 m^2 mol^{-1} and $\lambda_{max,2}$ = 440 nm (ε = 1590) whereas in n-hexane the corresponding values are $\lambda_{max,1}$ = 617 nm (ε = 2760) and $\lambda_{max,2}$ = 447 nm (ε = 2540).[5] Since the impurities in dithizone tend to absorb below 550 nm, the 'peak ratio' $R = A_{max,1}/A_{max,2}$ is a sensitive means of confirming the purity of a sample of dithizone (or that of one of its analogues) and of following the course of successive stages of purification, when R should increase to a constant value. Irving[5] has suggested that on these grounds alone, many of the extensive data published by Russian workers should be treated with considerable reserve.

Assuming that these two bands are due to the two species (1a) and (1b) in equilibrium, it is reasonable to identify the band of lower wavenumber with the thiol form [(40); R = SH], since formazans of the general

formula [(40); R = Cl or alkyl) have their main absorption band at ~420 nm[8] and the dithizonate ion [assumed to be (40); R = S^-] absorbs at 470 nm. There is commonly a bathochromic shift when chelating agents such as



(40)

acetylacetone, thenoyltrifluoracetone, 8-quinolinol, and 8-mercaptoquinoline form their metal complexes. Since metal dithizonates are known to be derived from the thiol form [since *S*-methyldithizone (4) behaves quite differently;[180] see also Figure 2], and since metal dithizonates possess a single absorption band in the region 450-550 nm, the change in spectrum on forming a metal complex might be explained by the disappearance of the thione band at ~620 nm and a bathochromic shift of the thiol band from ~420 nm. Thiobenzophenone and other thioketones have absorption bands near 600 nm, and the above allocations have been supported from studies of the spectra of 2-mercaptobenzothiazoles and thioquinolines and their *N*- and *S*-methyl derivatives.[167,181-183] The classical method for determining the structure in potentially tautomeric systems is to compare the parent substance with derivatives in which the structure has been locked unambiguously by methylation into one or other of the possible tautomeric forms. As explained in Chapter III, this fails with dithizone: only the *S*-methylated derivative

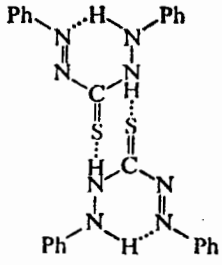
is known and this exhibits *syn-anti* isomerism about the :C=N- double bond accompanied by conspicuous changes in the visible spectrum.

Many of the doubts remaining about the existence of both thiol and thione forms in solution would be resolved if it were possible to study the properties of the *N*-methylated derivatives of dithizone, such as ArN(Me).-N(Me).CS.N:NAr', ArN(Me).NH.CS.N:NAr', and ArNH.N(Me).CS.N:NAr'. Many authors have attempted such syntheses without success,[37,84,179] but in Carlin's Ph.D. dissertation[70] it is stated that these compounds have been prepared by Barak and Corwin (Ar = Ph, Ar' = *p*-BrC_6H_4), and that various spectrophotometric parameters are reported and discussed. It is unfortunate that no details of this appear to have been published; nor can any of the authors concerned be traced.

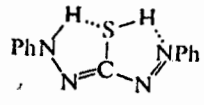
Pel'kis and Dubenko[184] have certainly accepted the hypothesis that solutions of dithizones contain thione and thiol forms in equilibrium, and have sought to calculate the percentage of each in terms of their extinction coefficients and from the spectrophotometric properties of the corresponding *S*-methyl derivatives. In calculating the ratio $\varepsilon_{on}/\varepsilon_{ol}$ (ε_{on} and ε_{ol} are the true extinction coefficients of the thione and thiol species, respectively, and these clearly differ from the observed values of $\varepsilon_{max,1}$ and $\varepsilon_{max,2}$) they assumed ε_{ol} to be identical with ε_{max} for *S*-methyldithizone, but they did not state which isomeric form they had chosen, or give details of the numerical values used. Their calculations led to the conclusion that $\varepsilon_{ol} = \varepsilon_{on}$ and this had the same value for all solvents. Irving[5] has shown that while it is clear that the value of the peak ratio, *R*, must reflect the position of a thiol-thione equilibrium, it cannot be taken as a precise measure of this unless $\varepsilon_{on} = \varepsilon_{ol}$ or the ratio $\varepsilon_{on}/\varepsilon_{ol}$ is uninfluenced by the solvent. That

the relative amounts of the tautomeric components are similarly affected by solvent-solute interactions is illustrated by the correlation of the peak ratios for dithizone with the peak ratios in the same 13 solvents for 1-(4-methoxy-3,5-dimethyl)-phenylazo-2-naphthol, a compound which has been formulated as forming azo- and hydrazo-tautomers in solution.[167,183]

The previous Chapters have shown that all formazans exist in a number of forms, due to isomerization about the -N=N- and :C=N- double bonds. For the thiol form of dithizone these could be [(2a), (2e), (2g), or (2i); $R^1 = R^2 = Ph$, $R^3 = SH$], though 12 additional structures could arise from rotation about single bonds and a further 48 forms in which charge-separations have given rise to zwitterions.[70] Many of these can be excluded straightaway on steric or other grounds. The thione-form of dithizone can also be represented by at least 16 forms in which there is no charge separation. Carlin[70] considered the alternatives in the light of optical, i.r., and some rather poor n.m.r. spectra, and concluded that solutions of dithizone contained a thione-dimer (41) and a thiol form (42).[70] Here again, the work has not been reported in the open literature. The full argument is too long and detailed to reproduce here and relies heavily on inferences drawn from the spectroscopic properties of related and model compounds. It should be noted that Carlin ascribed the long-wavelength band to the thiol form while the short-wavelength one is ascribed to the dimer, although there is no evidence of dimerisation in solution or in the solid state.

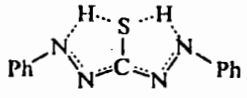


(41)

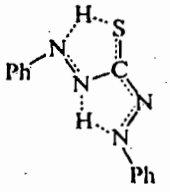


(42)

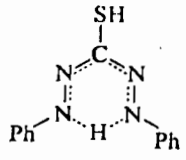
More recently (1970), Coleman, Foster, Kazan, and Mason[185] were unable to obtain the n.m.r. spectrum of dithizone itself owing to its low solubility, but by using the more soluble homologue 1,5-di(*o*-ethylphenyl)-thiocarbazone in $CDCl_3$ they observed 6 methyl protons at δ 1.4, 4 methylene protons at δ 3.0, 8 aromatic protons at δ 7.33 and 8.1, and 1.6 protons at δ12.03. The signal at δ12.03 showed no evidence of splitting over the range +50 to -45°C in $CHCl_3$ (in fact it sharpened at lower temperatures) and disappeared on adding CH_3OD. They interpreted their data as favouring a single symmetrical structure (43) (as subsequently found for solid dithizone), rather than rapid exchange between a form containing SH and a form containing NH. They also suggested (44) as the structure of a red metastable form (λ_{max} 550 nm) that they observed when a green solution of chloroform in a dry non-polar solvent was subjected to intense irradiation with a near-infrared tungsten lamp. They discount the idea of a thiol-thione equilibrium and state that 'although we have observed... solvent effects... they appear to be complicated by acid-base equilibria, trace metal effects and even oxidative decomposition of the dithizone'.



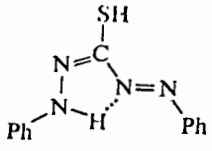
(43)



(44)



(42a)



(42b)

It is interesting that Coleman *et al.* only observed 1.6 protons at δ 12.03 in place of the expected total of 2.0 protons. Nabilsi[168] found that the n.m.r. spectrum of dithizone in $CDCl_3$ presented two signals, at δ 12.61 and δ 0.97, of integrated area 3 : 1, and completely accounting for the two non-aromatic protons. He observes that the signal at δ 0.97 occurs in the characteristic region for the SH group in the absence of significant hydrogen bonding. The lack of infrared absorption in the region 3100 - 3500 cm^{-1} indicates the absence of a free :NH group and implies its participation in strong hydrogen bonding. Nabilsi concludes that the thiol form (comprising about 25% of the total in $CDCl_3$) has the (mesomeric) structure (42a) or, less likely, (42b) whereas the thione form could be (43) or (44). It may be noted that if the ratio [thione]/[thiol] = 3 : 1 indicated by Nabilsi's[168] n.m.r. spectroscopy in $CDCl_3$ is compared with the peak ratio R = 2.59 for $CHCl_3$, there does seem some justification for using the latter as a direct measure of the tautomeric equilibrium constant.[5]

Following on the large literature of dithizone which regards this reagent as existing in solution in an equilibrium between thiol and thione forms, it seems quite audacious to deny the existence of this tautomerism. However, the few simple n.m.r. experiments reported in the following Section of this Chapter provide strong evidence for the existence of a

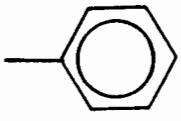
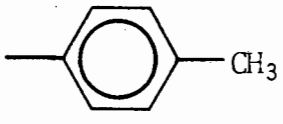
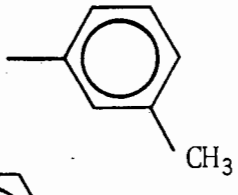
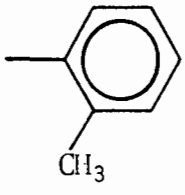
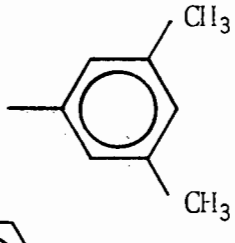
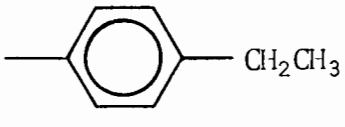
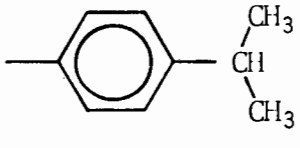
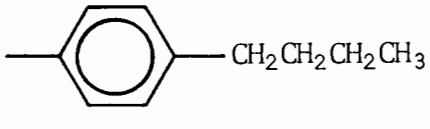
single structure in solution similar to that found in the solid state, *viz* structure (1c). A few comments on the compounds prepared in this work will be appropriate first.

Preparative work

Several homologues of dithizone substituted in the rings with alkyl groups (Table 31) were synthesized by Bamberger's route[3,178] from the corresponding 3-nitro-1,5-diarylformazans, most of which had been prepared for the work reported in Chapter II. The small yields (ca. 1%) of the nitroformazans with methyl groups in the 2- and 6-positions [(14) and (15)] reported in Chapter II did not allow the synthesis of the corresponding dithizones. The substituted dithizones were synthesized with the object of examining their ^1H n.m.r. spectra, especially with a view to determining the exact integral of the NH peak by reference to the well-defined integrals of, *e.g.*, methyl groups. (Nabilsi's[168] spectrum of dithizone showed only 1.5 protons at δ 12.61, but the integral was measured relative to the aromatic proton signal, under which would be any residual $CHCl_3$ protons from the $CDCl_3$ n.m.r. solvent.) In addition the equivalence, or otherwise, of aryl groups was expected to be made easier to observe by monitoring the substituent resonances as the temperature was decreased. The availability of Fourier Transform n.m.r. spectrometers has meant that for the first time reliable n.m.r. measurements may be made on the dithizones without having to worry about their low solubility in respect of the concentrations required for conventional continuous wave n.m.r. spectrometers.

Reduction of the nitroformazans to the corresponding thiocarbazides [as (39)] was carried out in good yield by using an excess of ammonium sulphide, and the final oxidation of the thiocarbazide to the correspon-

TABLE 31 : SYMMETRICAL 1,5-DIARYLTHIOCARBAZONES SYNTHESIZED IN THIS WORK

Number	Aryl group
(1)	phenyl 
(45)	*p*-tolyl 
(46)	*m*-tolyl 
(47)	*o*-tolyl 
(48)	3,5-dimethylphenyl 
(49)	*p*-ethylphenyl 
(50)	*p*-isopropylphenyl 
(51)	*p*-n-butylphenyl 

ing dithizone was carried out with methanolic potassium hydroxide. This is actually a disproportionation reaction and the maximum yield of thiocarbazone can be only 50%. It was found that yields of 80-95% of the thiocarbazone can be obtained by smooth oxidation of the thiocarbazide. The thiocarbazide is dissolved or suspended in ether or, better, carbon tetrachloride and air is slowly bubbled through the solution until the production of a very deep green colour indicates complete oxidation. Recalcitrant thiocarbazides may require reflux temperatures for acceptably rapid oxidation. Purification by column chromatography is necessary as oxidation of the thiocarbazone results in small quantities of the corresponding 2,3-diaryl-2*H*-tetrazolium-5-thiolate (32) in the product. However, chromatographic purification of the product resulting from the oxidation using methanolic potassium hydroxide is also necessary. Spectroscopically pure dithizones are usually prepared[181] by an extensive series of extractions from chloroform into dilute aqueous base, washing the acqueous layer with more chloroform, and re-extraction into chloroform or precipitation from the aqueous phase by acidification. In this work it was found that column chromatography provided a cleaner, quicker method of purification with a greatly enhanced yield. The peak ratio $R = A_{620}/A_{450}$ of dithizone purified by this method was 1.70 in CCl_4, which is indicative of pure dithizone.[5] After initial elution with benzene on a neutral alumina column the solvent is gradually changed to acetone and the dithizone band is washed off the column with 1% sodium bicarbonate solution in water. Acidification of the eluent yields the blue-black precipitate which may be collected by filtration. This method also avoids the necessity of evaporating off the solvent to recover the product; evaporation of solutions of thiocarbazones even at room temperature usually

results in the formation of small amounts of oxidation products such as (32). Details are given in the Experimental Section.

The dithizone labelled at N(1) and N(5) with 96 atom-% ^{15}N was synthesized by this route using the smooth oxidation procedure, and a sample of the ^{15}N-labelled thiosemicarbazide was kept aside for n.m.r. spectroscopy. It was hoped to observe the ^{15}N nuclei directly by ^{15}N m.m.r. spectroscopy, and this combined with the effect of ^{15}N on the ^{1}H n.m.r. spectrum of directly bonded protons would give insight into the structure of dithizone in solution. Several 'dummy runs' with unlabelled materials were attempted in order to optimize reaction conditions and obtain a good yield from the labelled nitroformazan synthesized for the work reported in Chapter II. A second route was investigated to obtain the ^{15}N-labelled dithizone which avoids the reduction and low yield oxidation steps of Bamberger's synthesis. In this route[186] the reactivity of the halogen atom in 3-chloro-1,5-diphenylformazan (52) was exploited in the reaction with sodium hydrogen sulphide to obtain the dithizone directly either by mechanical shaking at room temperature or by heating under reflux with NaHS. The 3-chloro-1,5-diphenylformazan (52) was obtained by coupling a benzenediazonium solution with dipotassium chloromalonate, prepared from the chloro-ester which resulted from the action of sulphuryl chloride on diethyl malonate (see over). This method, however, gave an overall poorer yield in trial runs than the route from the nitroformazan, especially if the smooth oxidation process was used in the latter route, and so was discarded as a route to the isotopically labelled dithizone. Again details will be found in the Experimental Section.

$$CH_2(CO_2Et)_2 \xrightarrow{SO_2Cl_2} ClCH(CO_2Et)_2 \xrightarrow[EtOH,\ 0°C]{KOH} ClCH(CO_2K)_2$$

$$ClCH(CO_2K)_2 + 2PhN_2^+ \longrightarrow PhN{:}N.C(Cl){:}N.NHPh \qquad (52)$$

$$PhN{:}N.C(Cl){:}N.NHPh \xrightarrow{NaHS} PhN{:}N.C(SH){:}N.NHPh \qquad (1b)$$

A modified form of Fischer's original synthesis of dithizone[1,179,187] was used to synthesize the $^{13}C(3)$ analogue of dithizone from 91 atom-% $^{13}CS_2$ and phenylhydrazine. In this modification the complete synthesis was carried out in a single vessel (a so-called 'one pot reaction') with a view to conserving valuable labelled material. If dithizone exists in solution as an equilibrium of thiol and thione tautomers, there should be a large difference in chemical shift of the ^{13}C resonance in $\gtrless C{=}S$ as opposed to $\gtrless C\text{-}SH$, and at low temperatures if the equilibrium is slow enough one might even observe two separate resonances. Because of the low solubility of dithizone, however, if spectra are to be obtained in a reasonable time even using Fourier Transform instrumentation, the carbon nucleus to be observed must be enriched with ^{13}C. Fischer's original method (unmodified)[1,187] was also used in an attempt to synthesize the 2,6-dimethylphenyl and 2,4,6-trimethylphenyl homologues in the 1,5-diaryl-thiocarbazone series, since the tiny yields of the corresponding nitro-formazans (14) and (15) obtained earlier (Chapter II) were not enough to proceed with Bamberger's general synthesis of the thiocarbazones. While the 2,6-dimethylphenylhydrazine was successfully prepared,[90] its reaction with CS_2 resulted in an intractable tar and it was not thought worthwhile to pursue the synthesis of these two homologues.

If dithizone exists in solution in tautomeric equilibrium between thiol and thione forms, then there should also be a distinction between the sulphur chemical shifts in $\rangle C{=}S$ and $\rangle C{-}SH$ which might be observable under suitable conditions. Unfortunately the only n.m.r. active isotope of sulphur is ^{33}S and this is a quadrupolar nucleus which suffers from very low natural abundance and relatively low sensitivity. Selenium, on the other hand, has a spin-$\frac{1}{2}$ isotope, ^{77}Se, with a natural abundance of 7.58% and an n.m.r. sensitivity of 6.97×10^{-3} with respect to the proton at constant field; this nucleus is observable with a pulse FT n.m.r. spectrometer having a tunable probe. The selenium analogue of dithizone, 3-seleno-1,5-diphenylformazan ('selenazone') has been synthesized by Ramakrishna and Irving.[35] Selenazone was synthesized in this work in the hope of obtaining a ^{77}Se spectrum which might throw light on the structure of the parent compound, dithizone, in solution. A modification of Bamberger's route was used, treating 3-nitro-1,5-diphenylformazan with ammonium selenide and oxidizing the resultant selenocarbazide in the usual way, but with due regard for the sensitivity of selenazone to moisture and air. Dimethylselenide was synthesized as the n.m.r. reference compound by reducing powdered selenium metal in an alkaline solution of sodium formaldehydesulphoxylate and reacting this with methyl iodide, as described by Bird and Challenger.[188] Details are reported in the Experimental Section of this Chapter.

2. Spectroscopic studies

The visible absorption spectra of the 1,5-diarylthiocarbazones (1) and (45) - (51) have been reported in the literature.[5,182,184,189,190] They all show two peaks, one close to 450 nm and one at 620 nm, with the peak ratio $R = A_{620}/A_{450}$ for chloroform solutions varying from 2.59 (dithizone) to 3.95 (*p*-n-butyl homologue). As a preliminary to n.m.r. work it was established that the absorption spectrum of dithizone in $CHCl_3$ solution was identical to that in $CDCl_3$. A proton n.m.r. spectrum of dithizone (1) in $CDCl_3$ was run without TMS added and this showed only two signals: a complex multiplet in the aromatic region and a singlet in the NH region which integrated for just less than 2 protons relative to the aromatic protons. While the use of FT n.m.r. spectroscopy makes it possible to observe good spectra of the relatively insoluble dithizones, it must be remembered that residual protons from the deuterated solvents also give rise to enhanced signals. Thus there is a residual $CHCl_3$ line underneath the aromatic proton signal and the intensity of other signals relative to this will be underestimated. For this reason alone the alkyl-substituted dithizones are useful in providing well-defined lines for integration reference. In the spectrum of dithizone (Figure 22) the baseline is undisturbed in the region in which SH resonances are found (δ 1 - 4) and there is no evidence of Nabilsi's[168] SH peak at δ 0.97. From the spectrum reproduced in his thesis, it appears that this peak is due to an impurity in the solvent or even a spinning side-band of an intense TMS resonance.

The ^1H n.m.r. spectral data for the alkyl-substituted dithizones in $CDCl_3$ are set out in Table 32 and the spectra are reproduced in Figure 23. These spectra show that the alkyl substituent groups, and thus the two

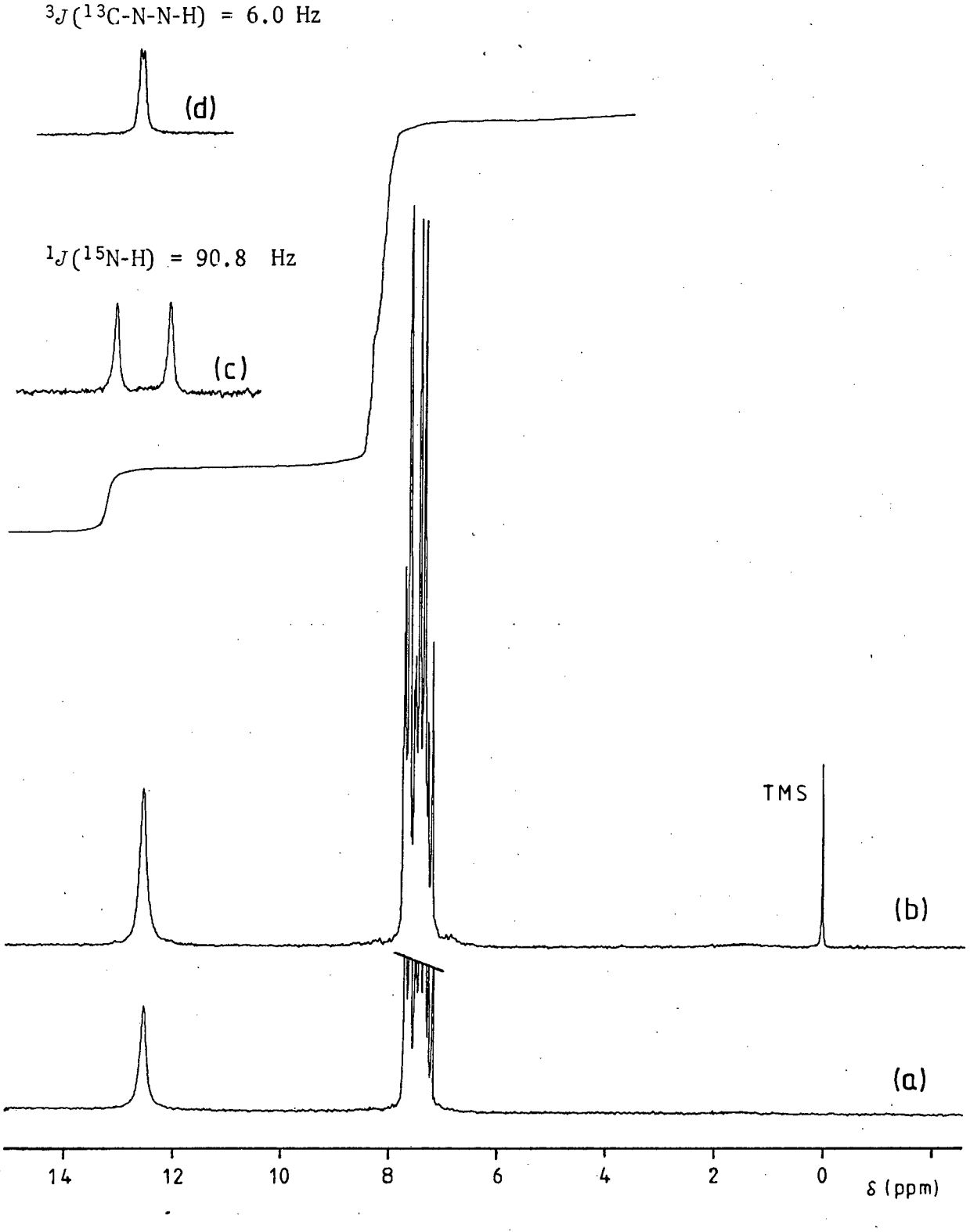


FIGURE 22 : ^{1}H n.m.r. spectrum of dithizone (1) in $CDCl_3$: (a) no TMS added, (b) TMS added for reference, (c) labelled at N(1) and N(5) with 96 atom-% ^{15}N, and (d) labelled at C(3) with 91 atom-% ^{13}C.

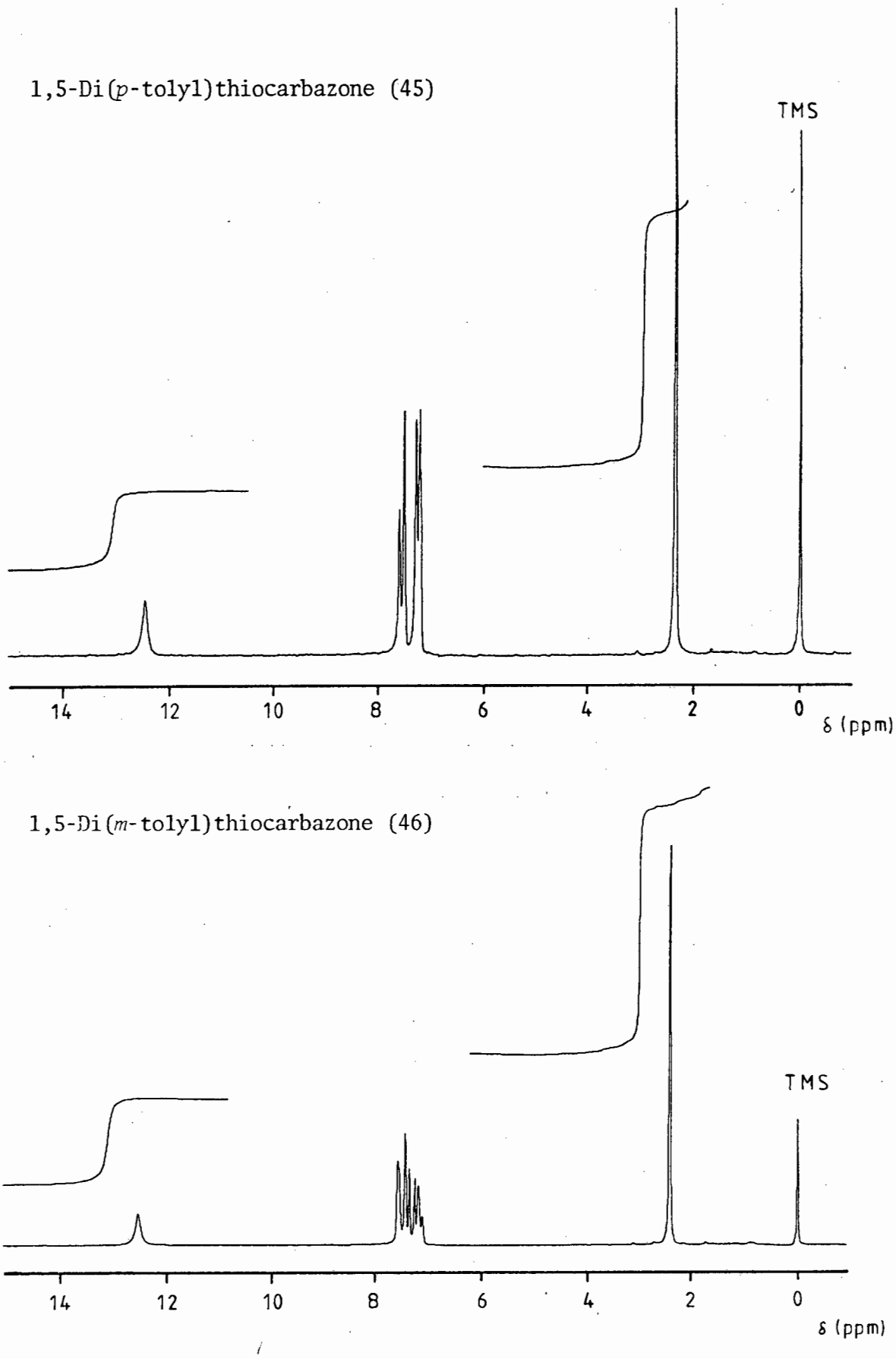
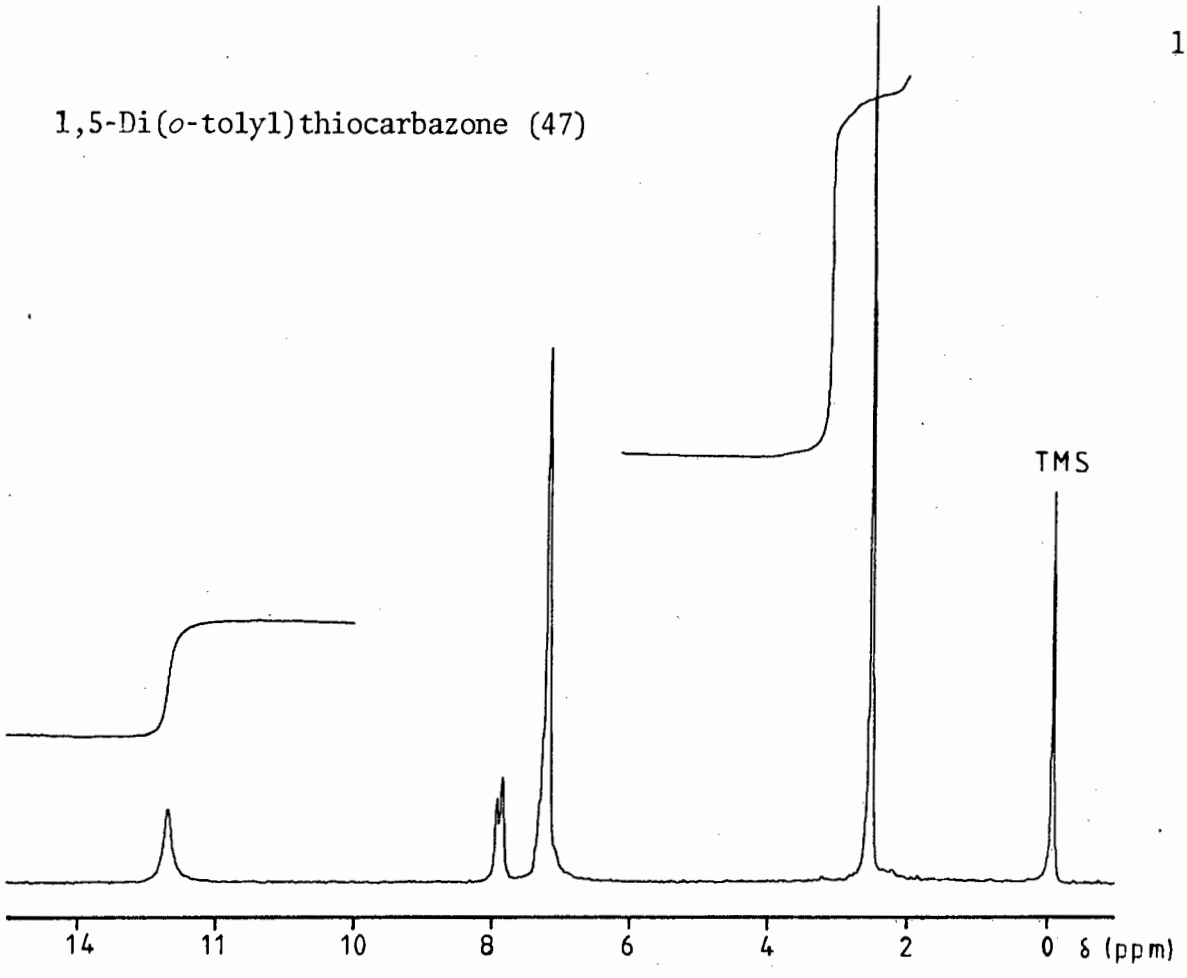


FIGURE 23 : ^{1}H n.m.r.spectra of the 1,5-diarylthiocarbazones (45) - (51) in $CDCl_3$.

1,5-Di(*o*-tolyl)thiocarbazone (47)



1,5-Di(3,5-dimethylphenyl)thiocarbazone (48)

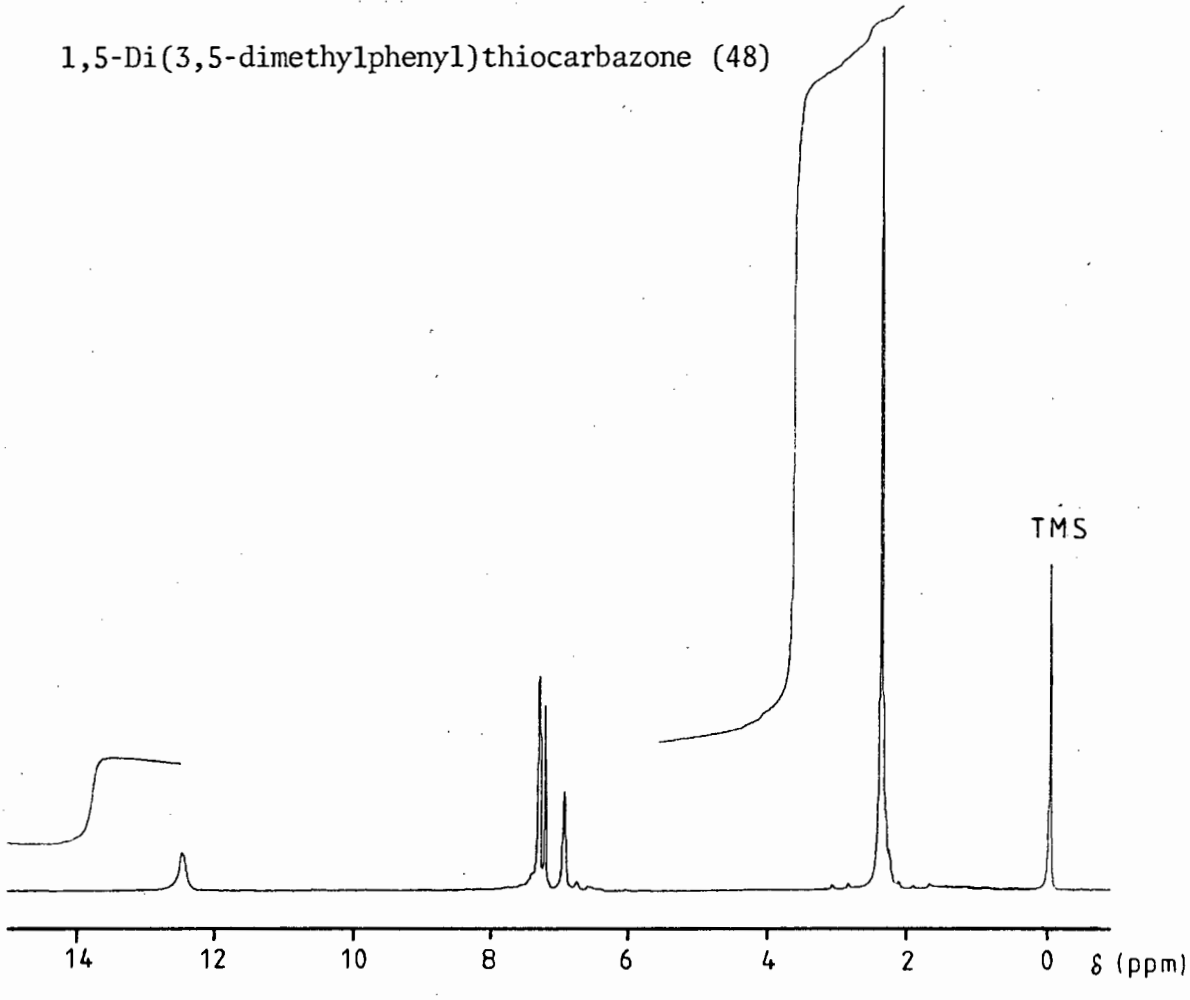


FIGURE 23 (Continued)

1,5-Di(*p*-ethylphenyl)thiocarbazone (49)

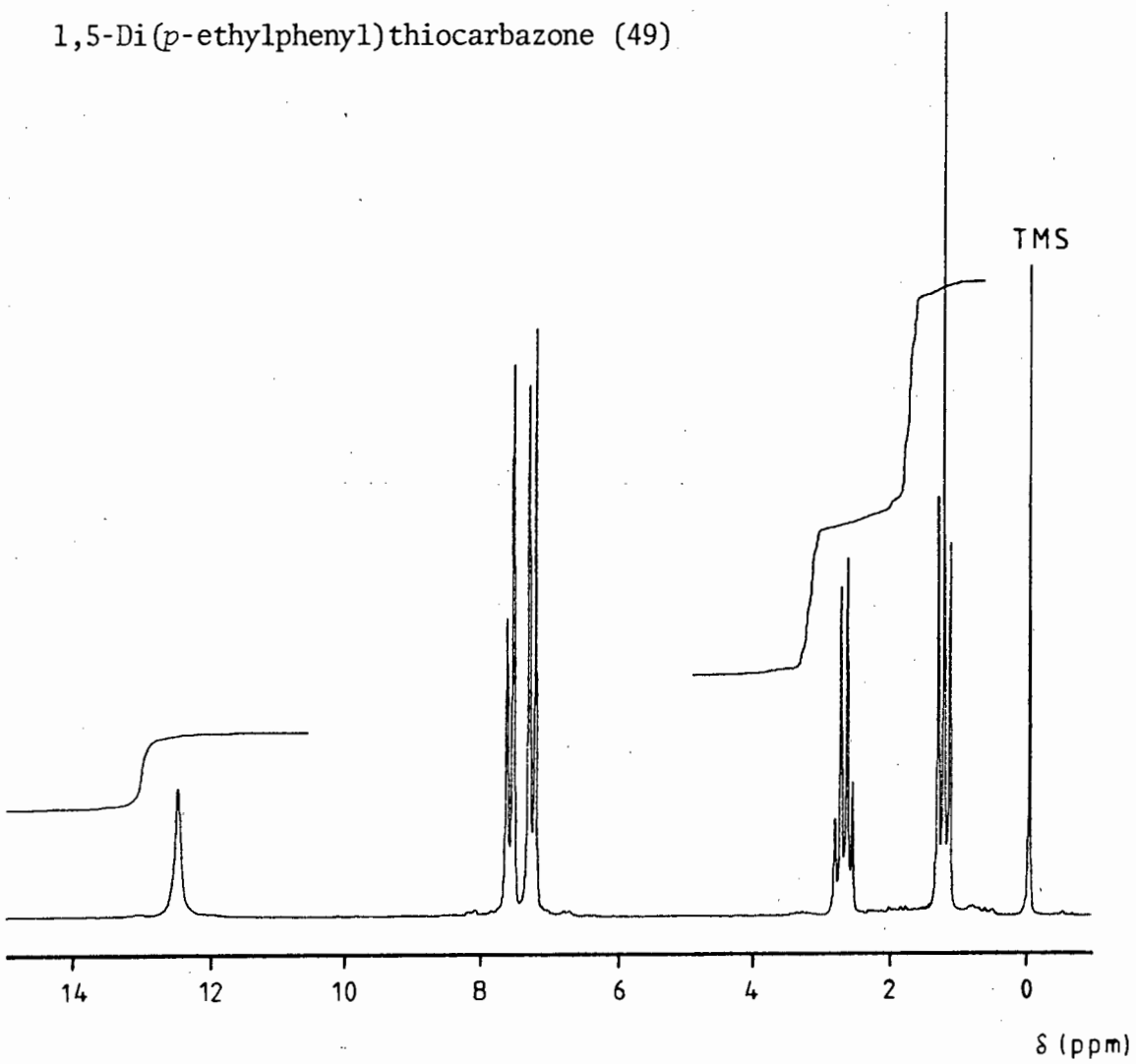


FIGURE 23 (Continued)

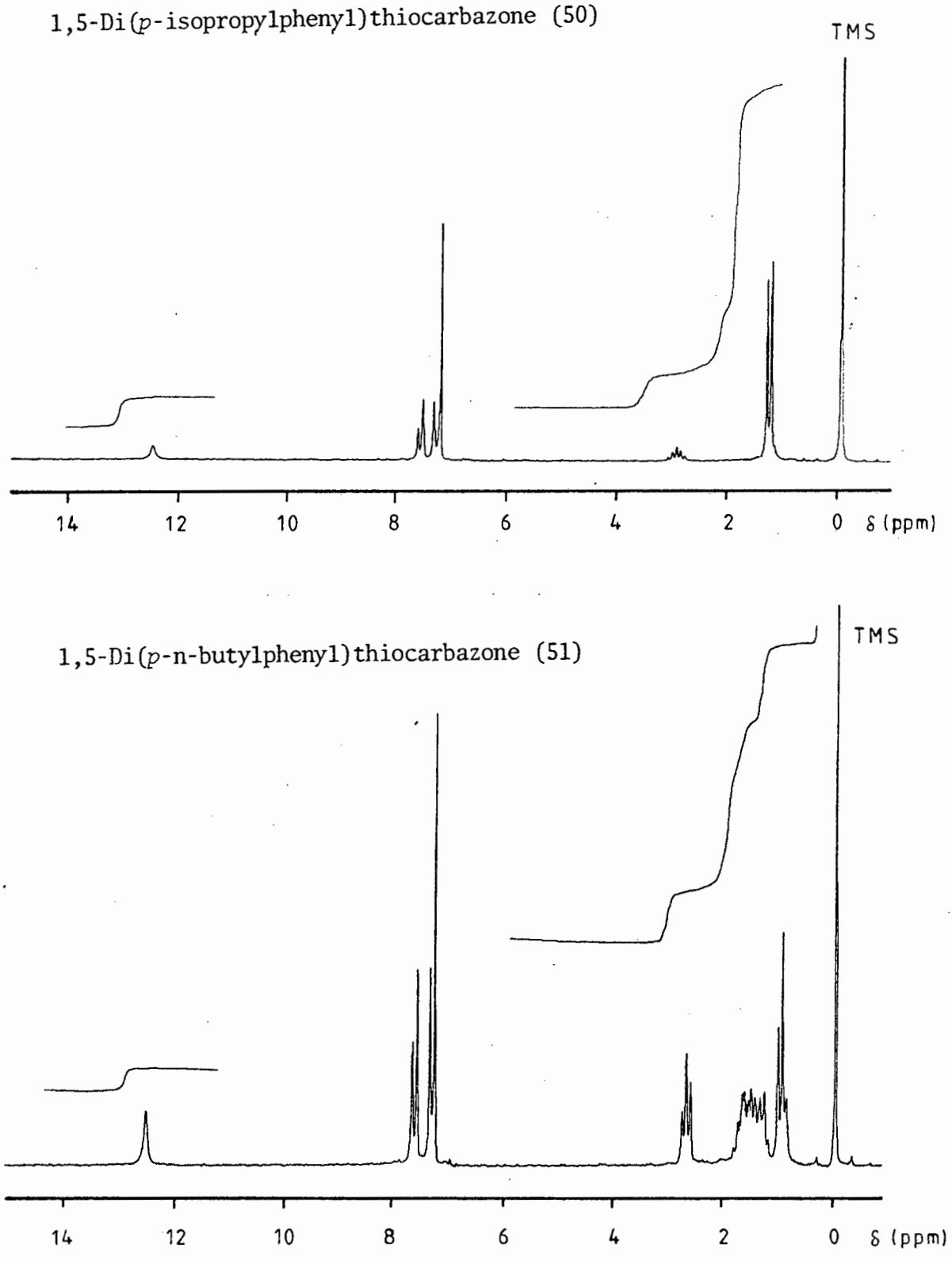


FIGURE 23 (Continued)

aromatic rings, are equivalent on the n.m.r. time-scale, and the structure of the molecules in solution must be symmetrical; alternatively, we may be observing the time-average signal from two different species in equilibrium. The same effect may be seen in the aromatic proton resonances themselves in the case of the *para*- and 3,5-substituted rings, where simple patterns result. In each case, the singlet in the NH region at about δ 12.5 integrates for *exactly* 2 protons (see Figure 23) and the signal disappears completely immediately upon washing with D_2O. None of the signals in the spectra of (1) and (45) - (51) is affected by running the spectra at either -50°C or +60°C, beyond the slight narrowing and broadening of lines expected at low and high temperatures, respectively.

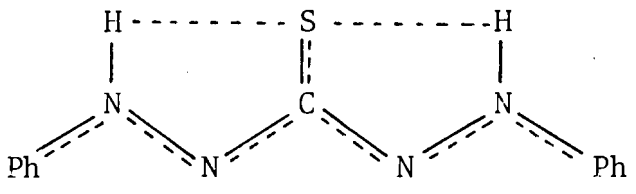
Table 32 also gives data for the spectra run in deuteroacetone and deuterobenzene. Again equivalence of the alkyl substituents is observed and all the above remarks apply to these spectra as well, except that the singlets in the NH region in the acetone spectra integrate for less than 2 protons. No new peaks appeared to account for the missing fractions of protons and it is believed that exchange must have occurred with D_2O in the not completely dry $(CD_3)_2CO$. It is not unusual to find traces of D_2O in n.m.r. solvent deuteroacetone,[191] and the effect of its presence is accentuated by the dilute solutions afforded by the thiocarbazones in these solvents. In benzene solutions the corresponding singlets integrated for exactly 2 protons.

There can be no doubt that both protons are bound to equivalent nitrogen sites, *viz* N(1) and N(5). When the ^1H spectrum of the analogue of dithizone labelled at N(1) and N(5) with ^{15}N is measured, the NH singlet at δ12.60 is split into a doublet with a normal[158] N-H coupling constant

of 90.8 Hz (Figure 22). This value excludes the possibility of any rapid tautomeric equilibrium, such as a thiol-thione system. In such a system the observed spin coupling constant, J(obs), is given by a weighted average of the various coupling constants involved,[156,192] in that case ^{1}J(S-H) and $^{1}J(^{15}$N-H). If P(S) and P(N) represent the mole fractions of the two tautomeric species, then

$$J(\text{obs}) = {}^{1}J(\text{S-H}).P(\text{S}) + {}^{1}J(^{15}\text{N-H}).P(\text{N})$$

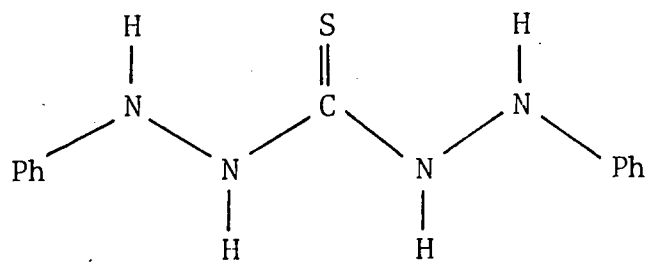
and if ^{1}J(S-H) is assigned a value of zero and $^{1}J(^{15}$N-H) of an unperturbed N-H bond is assumed to be *ca.* 90 Hz,[158] then it is clear that since P(N) is 1, the proton is bonded to N all the time and only one species exists. In this way the positions of the keto-enol equilibria in Schiff bases have been determined,[156] and the predominance of the enamine-thione tautomeric form in methyl dithioates has been established.[193] In Chapter III $^{1}J(^{15}$N-H) was found to be 92.2 Hz for the yellow *anti*,s-*trans* form of *S*-methyldithizone (4f), for which certainly only one form is possible. The splitting of the ^{15}NH peak with no residual line indicates that the protons are equivalent and must be attached to N(1) and N(5), and the probably planar structure (1c), as found by X-ray crystallography in the solid state, is proposed for the structure of dithizone in solution.



(1c)

It will be noted in Table 32 that while the chemical shifts of lines from the thiocarbazones in chloroform and acetone are very similar, the lines from benzene spectra are consistently about 0.5 ppm upfield (or about 0.3 ppm downfield for NH lines). These shifts are expected on changing to an aromatic solvent and certainly do not correlate with the peak ratios $R = A_{620}/A_{650}$ in the visible spectra. Steric interaction between the NH protons and the *o*-tolyl methyl groups in (47) is probably responsible for mutual van der Waals deshielding and the observed downfield shift of the NH and CH_3 resonances compared with these lines in the other derivatives.

The ^1H n.m.r. spectrum of diphenylthiocarbazide, which is known to have the structure (38) in the solid state,[194] was obtained in spite of the low solubility of the compound in $CDCl_3$. Two NH resonances were found, one at δ 6.18 and one at δ 8.08, each integrating for 2 protons. Both resonances disappeared on washing with D_2O. The compound labelled at



(38)

N(1) and N(5) with ^{15}N was then run, and the NH singlet at δ 6.18 split to give a doublet with $^1J(^{15}N\text{-}H) = 85.2$ Hz. Clearly the protons attached

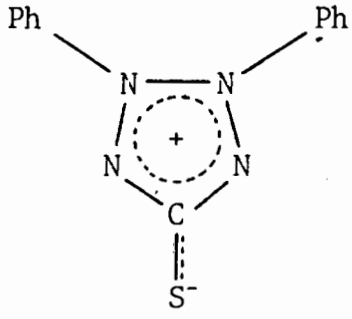
to N(1) and N(5) are not involved in intramolecular exchange, whereas this is still possible for the protons attached to N(2) and N(4). Whether a thione-thiol equilibrium exists when this compound is dissolved in chloroform could be tested by labelling N(2) and/or N(4) with ^{15}N and observing the magnitude of the ^{15}N-H coupling constant.

Unfortunately, although much effort was spent in attempts, no ^{15}N n.m.r. signals were observed from the ^{15}N-labelled dithizone in chloroform. For ^{15}N with protons attached relaxation times for the nucleus are of the order of 10 seconds at normal probe temperatures and increasing up to as much as 60 seconds for tertiary nitrogens.[195] Since a delay of at least 5 times the relaxation time of the nucleus is required between each pulse,[163] collection of data for ^{15}N spectra is slow unless shiftless relaxation agents like chromium(III) acetylacetonate are used. Their use in this study of dithizone was prohibited because of the need to exclude impurities. Spectra were run with broad-band ^{1}H-decoupling without observing any signals after overnight scans, and since it is known that nuclei with negative gyromagnetic ratios (such as ^{15}N) can often have their signals decreased in intensity or completely lost (nulled) due to the nuclear Overhauser effect,[163] spectra were also run using inverse-gated ^{1}H-decoupling where the decoupler cycle time is adjusted so that the partial NOE which develops during the acquisition time decays again during the delay time. However, no signals were observed. On the other hand, as seen above, the ^{15}N-labelled compound did provide useful information in the proton spectrum of dithizone.

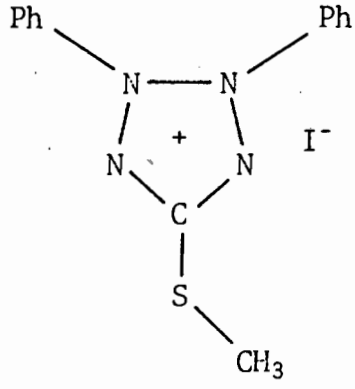
More success was achieved with the ^{13}C n.m.r. spectra of ^{13}C-labelled dithizone and its derivatives. If dithizone existed in solution in both thiol and thione forms one might expect the ^{13}C resonances of $\diagup\!\!=\!\!\diagdown$C-SH

and $\rangle$C=S to be individually observable if the equilibrium was slow enough. The thiol carbon would have a chemical shift in the region δ 54 - 72 ppm downfield of TMS, whereas the thione carbon resonance would be found in the region δ 180 - 200 ppm[161] In fact a single peak is observed in the ^{1}H decoupled spectrum at δ 171.4 which does not shift or split at -50°C (Figure 24). This chemical shift may be compared with that of Et·NH·C(S)·NH·Et, in which the thiocarbonyl ^{13}C resonance is found at 182.8 ppm;[161] presumably the C=S bond order is larger in this compound. The coupled spectrum (Figure 24, inset) shows a triplet (1 : 2 : 1) with 6.0 Hz coupling to the equivalent NH protons through three bonds *i.e.*, $^{3}J(^{13}C\text{-}N\text{-}N\text{-}H)$. If the NH protons were not equivalent, and symmetrically situated about the $^{13}C(3)$ atom, a perfect triplet would not be obtained. The triplet is observed unchanged at -50°C. On washing with D_2O the triplet collapses to a singlet (Figure 24, inset). The 6.0 Hz coupling is also found in the proton spectrum of the ^{13}C-labelled dithizone (Figure 22), where the NH peak is split into a doublet; this spectrum also shows no changes at -50°C other than a slight narrowing of lines.

Oxidation of dithizone with potassium hexacyanoferrate(III) yields 2,3-diphenyl-2*H*-tetrazolium-5-thiolate ['dehydrodithizone; (53)], the structure of which has been confirmed as meso-ionic by *X*-ray crystallography.[196] The ^{13}C n.m.r. spectrum of this compound labelled with ^{13}C in the tetrazole ring (Figure 25) gives a single peak at δ 183.5 ppm downfield from TMS, providing the most deshielded of all the carbon resonances observed in this work, and indicative of the dipolar meso-ionic structure with a residual positive charge on the tetrazole ring.



(53)



(54)

When dehydrodithizone (53) is treated with methyl iodide, 5-methylthio-2,-3-diphenyltetrazolium iodide (54) is obtained. This was found to be very much more soluble in $CDCl_3$ than any of the other compounds for which ^{13}C spectra were obtained, and as a result the phenyl ring resonances are seen in the spectrum in addition to the ^{13}C-labelled tetrazolium ring carbon at δ 169.2 ppm (Figure 26). This line is shifted about 22 ppm downfield from the corresponding resonance in *S*-methyldithizone (4) due to the positive charge residing on the tetrazolium ring in (54). When the decoupler is switched off and data again accumulated the line is split into a quartet (1 : 2 : 2 : 1) by the $-SCH_3$ protons with $^3J(^{13}C\text{-}S\text{-}C\text{-}H)$ = 5.4 Hz (Figure 26, inset). Table 33 summarizes all the ^{13}C chemical shifts obtained in this work.

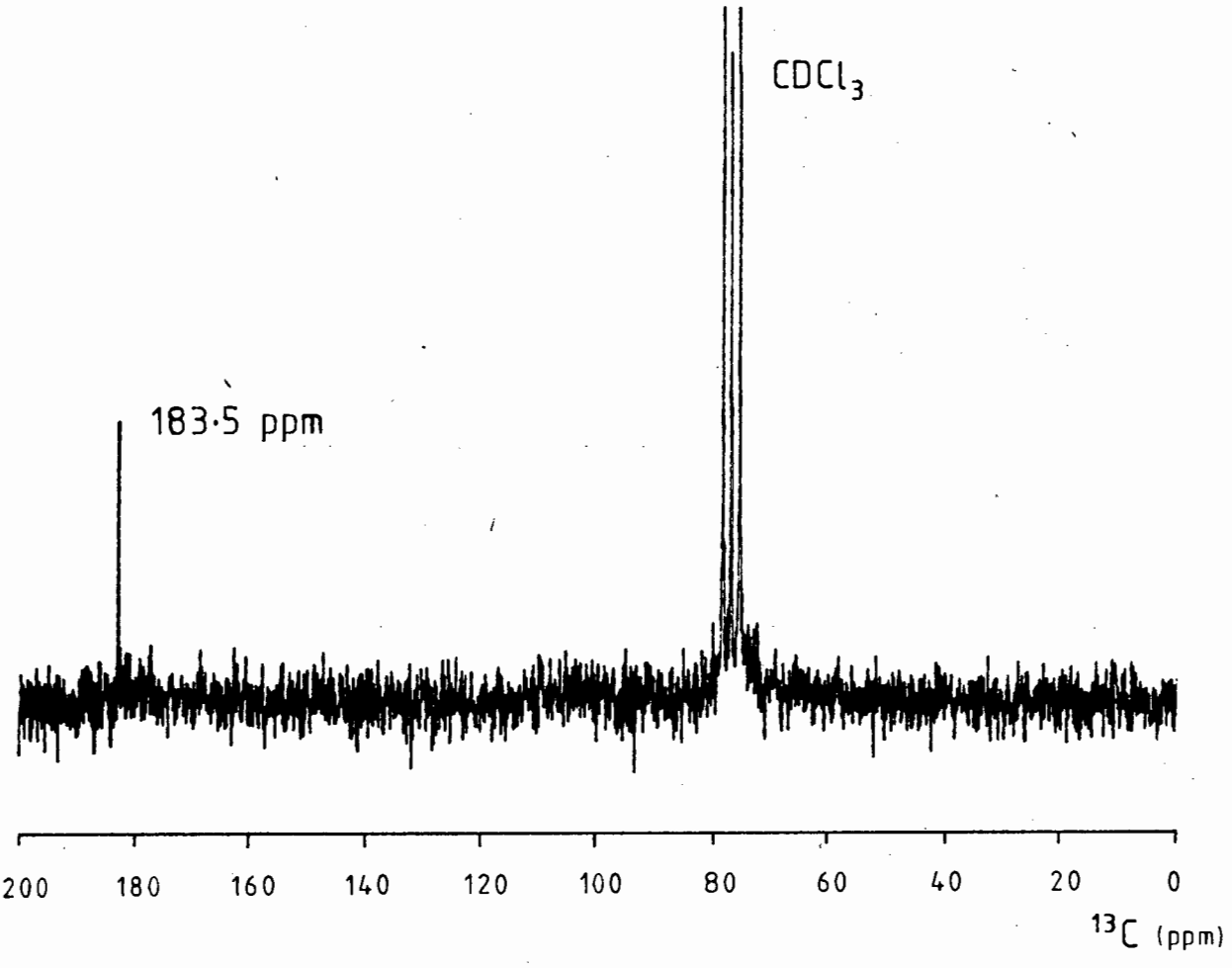


FIGURE 25 : ^{13}C n.m.r. spectrum of dehydrodithizone (53) labelled with 91 atom-% ^{13}C in the tetrazole ring in $CDCl_3$. Chemical shifts are downfield from external TMS.

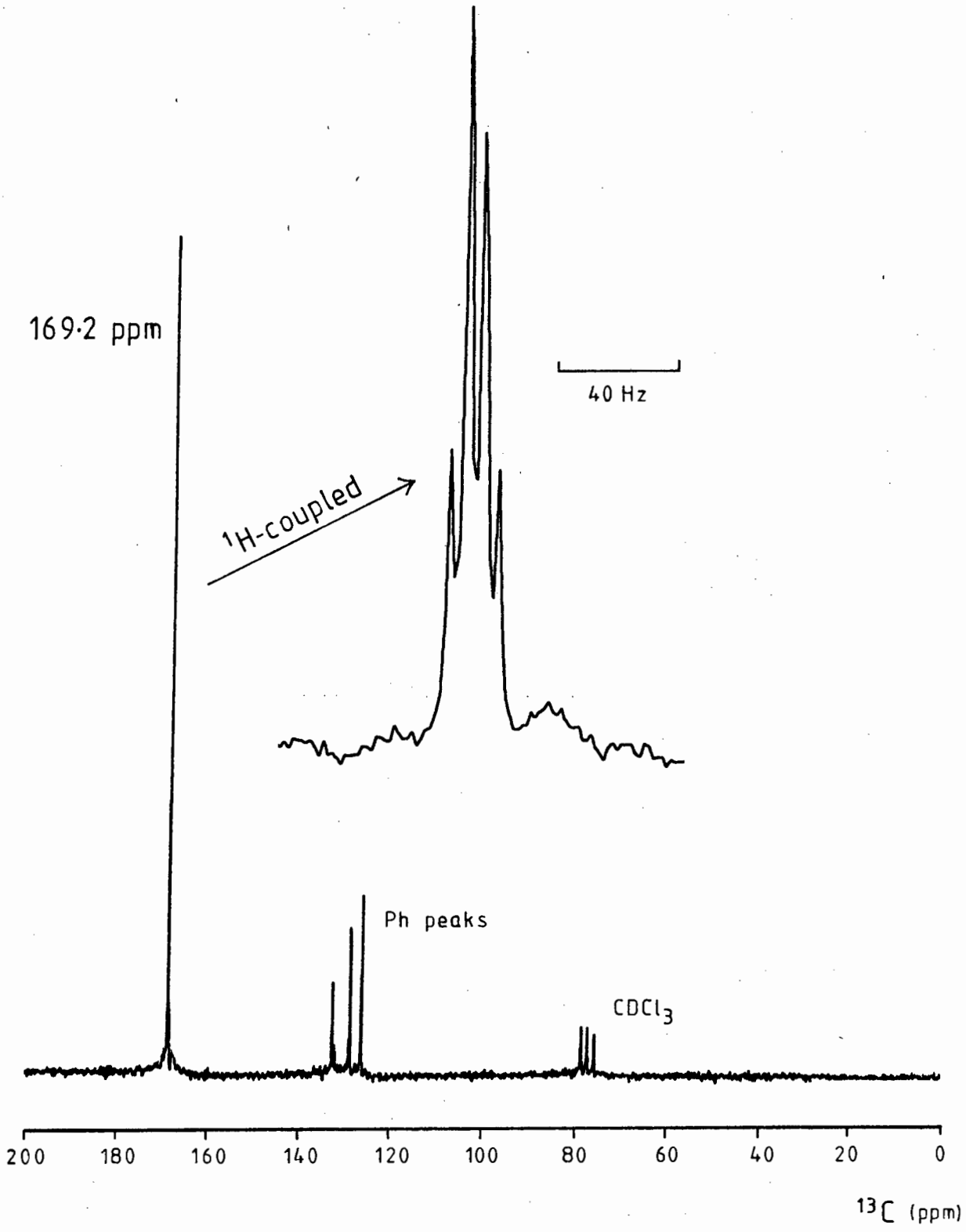


FIGURE 26 : ^{13}C n.m.r. spectrum (^{1}H-decoupled) of the tetrazolium iodide (54) labelled with 91 atom-% ^{13}C in the tetrazolium ring in $CDCl_3$. Chemical shifts are downfield from external TMS. Inset: ^{1}H-coupled resonance from the ^{13}C-labelled carbon showing quartet with $^{3}J(^{13}C\text{-}S\text{-}C\text{-}H) = 5.4$ Hz.

TABLE 33 : ^{13}C CHEMICAL SHIFTS OF LABELLED CARBON RELATIVE TO TMS (ALL IN $CDCl_3$ SOLUTION)

Compound	δ/ppm
S-Methyldithizone (4)	
syn,s-*cis* isomer	146.3
anti,s-*trans* isomer	147.4
5-Methylthio-2,3-diphenyltetrazolium iodide (54)	169.2
3-Nitro-1,5-diphenylformazan (9)	171.0
Dithizone (1)	171.4
Dehydrodithizone (53)	183.5

No ^{77}Se spectra were obtained for selenazone, the selenium analogue of dithizone, mainly because of the dilute selenazone solutions obtained in $CDCl_3$, together with the naturally low abundance of the ^{77}Se isotope (7.58%) and an n.m.r. sensitivity of 6.97×10^{-3} with respect to the proton at constant field. The dilute solutions used and the long relaxation time of the ^{77}Se nucleus(5 - 20 seconds)[197] necessitated accumulation of data over many hours. The selenazone could not be kept stable in solution for long enough to obtain a spectrum, and oxidation took place even when traces of reducing agents such as SO_2 were added to the solvent. Good ^{77}Se spectra of the reference compound, dimethylselenide, were obtained, however, from a 20% solution of $(CH_3)_2Se$ in $CDCl_3$. Since ^{77}Se n.m.r. spectra are rather uncommon the ^1H-coupled spectrum is shown in Figure 27, where it is seen that the heptet with $^2J(^{77}Se\text{-}C\text{-}H)$ = 10.0 Hz is nearly fully resolved. A sharp singlet was obtained in the broad-band ^1H-decoupled spectrum. The

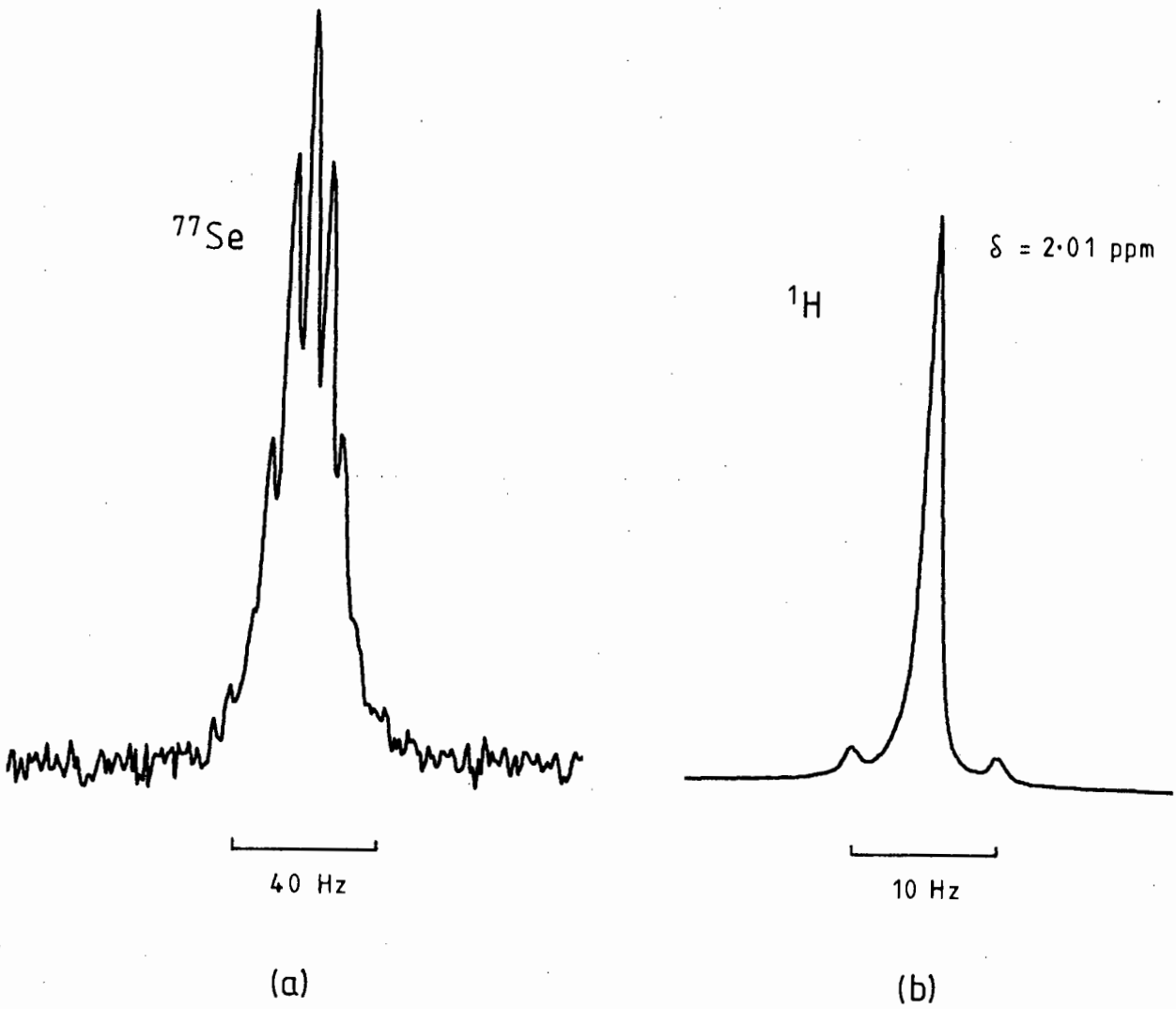


FIGURE 27 : (a) ^{77}Se n.m.r. spectrum of CH_3SeCH_3 in $CDCl_3$ showing a nearly fully resolved heptet with $^{3}J(^{77}S\text{-}C\text{-}H)$ = 10.0 Hz.

(b) ^{1}H n.m.r. spectrum of CH_3SeCH_3 in $CDCl_3$ showing ^{77}Se satellites with $^{3}J(^{77}S\text{-}C\text{-}H)$ = 10.0 Hz.

proton spectrum showed a singlet at δ 2.01 ppm flanked by ^{77}Se satellites 10.0 Hz apart (Figure 27). It is unfortunate that a ^{77}Se spectrum of selenazone was not obtained, for the position of its resonance in the large (*ca.* 1400 ppm) chemical shift range of ^{77}Se nuclei[197] could have provided a sensitive probe into the nature of selenazone in solution, which has similar visible spectral characteristics to dithizone, and which has been postulated as existing in a selenol-selenone tautomeric equilibrium.[35]

The ^{1}H n.m.r. spectra of the substituted dithizones (45) - (51) and the ^{13}C- and ^{15}N-labelled dithizones, as well as the ^{13}C n.m.r. spectra of dithizone and its derivatives, however, have provided enough evidence to discard the thiol-thione equilibrium hypothesis in favour of the single structure (1c). This is the same as that found in the solid state[10] and similar to that proposed by Coleman *et al.*[185] (43). Coleman has drawn the structure with dotted lines from the hydrogens to both nitrogen and sulphur [as (43)], implying two equivalent mobile hydrogen atoms, where as the ^{15}N-H coupling constant values indicate that there is a definite bond from N to H [as (1c)]. The hydrogens appear to be strongly hydrogen-bonded to the sulphur atom, however, and the detailed i.r. investigations reported by Kemula, Gańko and Janowski[198,199] show that the dithizones exhibit a broad band in the region 3100 - 2800 cm^{-1} with several absorption mixima. On deuteration this band disappears and a new broad band appears at about 2200 cm^{-1}, which is assigned to the N-D stretching mode; in the region 3100 - 3000 cm^{-1} only maxima corresponding to aromatic C-H stretches remain. No S-H stretching bands expected around 2600 cm^{-1} were found, and these authors claim that 'the similarity of the i.r. spectra of dithizone in solution and in the solid state denies the possibility of tautomerism', and they propose

Coleman's structure (43) as being consistent with their data.[199]

The diffuse reflectance spectrum of solid dithizone shows a clearly defined band at 450 nm, similarly situated to the shorter wavelength band in CCl_4 or $CHCl_3$; covering the region 580 - 610 nm is a broad shoulder which corresponds to the prominent peak at 620 nm in CCl_4 or 605 nm in $CHCl_3$. It appears that the known solid-state structure of dithizone, (1c), which gives rise to two bands in the diffuse reflectance spectrum (albeit one ill-defined) corresponding to the two bands in the solution spectrum, persists when the solid is dissolved in organic solvents. It is known[37] that the visible absorption spectrum of dithizone in solution does not change on decreasing the temperature to -48°C; the peak ratio *R* remains constant. This corroborates what was seen in the ^1H and ^{13}C n.m.r. spectra, which remained unchanged down to -50°C. These facts are also best interpreted in terms of the single structure (1c) in solution.

It is perfectly feasible for a single species in solution, such as (1c), to give rise to two intense bands in the visible spectrum. Recent workers[200] have approached the problem by calculating the energies and intensities of electron transitions of different forms of dithizone by molecular orbital theory (LCAO MO SCF LCI) and comparing calculated oscillator strengths at many wavelengths with experimentally determined spectra. Considerable success attended their calculation for the protonated species of dithizone, H_3Dz^+, in 60% H_2SO_4 and their calculations for the anion HDz and the possible anion Dz^{2-} seem not unreasonable. Their calculation for dithizone itself is based on the single thiol form (42), which has the same configuration as (1c) except that one of the hydrogens is attached sulphur, and predicts two bands in the visible part

of the spectrum (at about 440 and 740 nm) so that the simultaneous presence of the thione and thiol forms in dithizone solutions cannot be implied from the existence of these two bands alone.

Spěváček and Spěváčková[200] consider that the longer wavelength band in dithizone belongs to the electronic transition from the free electron pair of the sulphur atom to the first unoccupied π-orbital; it is the charge transfer from the sulphur atom to the π-orbital which is localized predominantly in the double bond between the nitrogen atoms. The shorter wavelength band they consider 'formed by the transition between the last but one occupied and the first unoccupied π-orbitals'. Whatever the source of the two bands in the absorption spectrum of dithizone, there can be no doubt that the relative peak heights do change from solvent to solvent. The postulated structure (1c) is open and planar, thus exposing the π-orbitals to electronic interactions from the various solvent molecules and possibly affecting the relative energies of the two transitions responsible for the observed absorption spectrum. While it would be satisfying to find another kind of molecule which exists in solution as a single species yet which also gives two peaks in the absorption spectrum whose intensities vary according to the solvent, the evidence presented in this Chapter for a single species of dithizone in solution [as (1c)] seems incontrovertible.

3. Experimental

General and spectroscopic

Visible absorption, diffuse reflectance, and n.m.r. spectra were generally measured on the same instruments and under the same conditions as the work reported in Chapters II and III. Special care was taken in cleaning the optical cells, the n.m.r. tubes, and the glassware in which solutions of thiocarbazones were handled. The cleaning was done as described in Chapter III. This provided metal-free glassware as tested by a very dilute solution of dithizone in chloroform, which remained pale green when used to rinse the glassware. A comparison of the visible spectrum of dithizone in $CHCl_3$ and $CDCl_3$ was made by purifiying a small quantity of dithizone by paper chromatography and extracting the pure dithizone spot into $CHCl_3$ in an optical cell (1 cm) and filling with $CHCl_3$ to a mark. After recording this spectrum the solvent was evaporated from the optical cell by careful application of a vacuum and the cell was re-filled to the mark with $CDCl_3$. The resulting spectrum was identical to the first.

Proton n.m.r. spectra were recorded on the Bruker WH-90DS pulse FT spectrometer at 90 MHz, the dilute solutions of dithizone and its derivatives requiring accumulation of about 20 transients. The Bruker variable temperature control provided sample temperatures down to -50°C. Care was taken to run the acetone spectra immediately after preparation so as to avoid the reported condensation of acetone with dithizones to form the corresponding thiadiazolines.[201] The ^{13}C spectra were recorded under similar conditions as used for the work reported in Chapters II and III, though in general more transients were collected (*e.g.*, 20000

for dehydrodithizone) due to the insolubility of the compounds. Deuterochloroform was used as solvent for all ^{13}C n.m.r. studies, and no other internal reference was used. The ^{15}N n.m.r. operational parameters were the same as described in Chapter II. Selenium-77 resonances were observed at 17.16 MHz on the Bruker instrument and satisfactory spectra of the reference compound, dimethylselenide (20% in $CDCl_3$), were obtained from 4000 transients using an estimated 30° pulse and 4 second cycle time. Spectra were recorded with and without noise-modulated ^1H-decoupling (1W, 3.3 kHz).

Preparations

General preparative procedures and facilities were unchanged from the work reported in Chapters II and III.

1,5-Di(*p*-tolyl)thiocarbazone (45)

3-Nitro-1,5-di(*p*-tolyl)formazan [(10); 8.0 g], obtained as described in Chapter II, was suspended in absolute ethanol (60 cm^3) in a 100 cm^3 round-bottomed flask and cooled to 0°C in an ice bath. Dry ammonia gas was bubbled through the mixture until it was saturated (20 minutes) and then hydrogen sulphide gas was passed into the solution until the thiocarbazide separated; the bubbling tube was used as a stirring rod. When reduction was complete as indicated by a change of colour from maroon to yellow and by disappearance of unreduced particles of the nitroformazan, the suspension was added in a thin stream to distilled water (200 cm^3) with mechanical stirring and immediately filtered off by suction on a Büchner funnel to remove 1,5-di(*p*-tolyl)thiocarbazide which was washed with water and dried over silica gel *in vacuo* (6.80 g, 88.3%). The surface of the dry powder slowly turned grey-green as oxidation took place.

The unstable thiocarbazide compound was oxidized at once to the thiocarbazone by treating with a 5% methanolic potassium hydroxide solution (30 cm^3) at room temperature. It was mixed well and lumps were broken up with the flat end of a stirring rod. A clear dark red solution was obtained which was immediately neutralized by pouring slowly into ice-cold dilute sulphuric acid (1 litre of 0.5 *M*) with vigorous mechanical stirring. After stirring for 1 hour the impure 1,5-di(*p*-tolyl)thiocarbazone was filtered off, washed with water, and dried over silica gel *in vacuo* (1.9 g, 28.0% based on thiocarbazide).

The crude product (1.0 g) was dissolved in the minimum amount of benzene and added to a chromatographic column (30 cm long, 2.5 cm diameter) of neutral alumina slurried in benzene. Elution with benzene produced a red fore-run. Once this was visibly separated from the dark band at the origin elution was continued with solutions of acetone in benzene, increasing the acetone concentration rapidly so that pure acetone was used to wash off the last of the red fore-run. A 1% solution of sodium bicarbonate in water was added to the column and the thiocarbazone fraction was poured in a thin stream into dilute sulphuric acid. After stirring for an hour the fine blue-black precipitate of (45) was isolated by filtration and dried over silica gel *in vacuo* (0.60 g, 60% based on crude product; m.p. 161-163°C decomp.). (Found: C, 63.15; H, 5.55; N, 19.75%. Calc. for $C_{15}H_{15}N_4S$: C 63.6; H, 5.3; N, 19.8%.)

1,5-Di(*m*-tolyl)thiocarbazone (46)

This was prepared in the same way as (45) above, starting from the corresponding nitroformazan (11), in 17.2% yield based on the thiocarbazide, which itself was obtained in 90% yield. The thiocarbazone melted at 154-158°C

(decomp.). (Found: C, 63.3; H, 5.4; N, 19.75%. Calc. for $C_{15}H_{15}N_4S$: C, 63.6; H, 5.3; N, 19.8%.)

1,5-Di(*o*-tolyl)thiocarbazone (47)

This was prepared from the nitroformazan (12) in the same way as (45) above, in 22.1% yield after purification (based on the thiocarbazide obtained in 92% yield). The pure (47) melted over the range 135-138°C (decomp.). (Found: C, 63.2; H, 5.45; N, 19.7%. Calc. for $C_{15}H_{15}N_4S$: C, 63.6; H, 5.3; N, 19.8%.)

1,5-Di(3,5-dimethylphenyl)thiocarbazone (48)

This was prepared from the nitroformazan (13) in the same way as (45) above, in 28.2% yield after purification (based on the thiocarbazide obtained in 86% yield). The pure (48) melted over the range 137-140°C (decomp.). (Found: C, 65.2; H, 6.1; N, 18.2%. Calc. for $C_{17}H_{19}N_4S$: C, 65.6; H, 6.15; N, 18.0%.)

1,5-Di(*p*-ethylphenyl)thiocarbazone (49)

This was a sample provided by Professor H.M.N.H. Irving. It was purified in the same way as (45) above, when it melted over the range 155-158°C (decomp.). (Found: C, 65.3; H, 5.9; N, 18.2%. Calc. for $C_{17}H_{19}N_4S$: C, 65.6; H, 6.15; N, 18.0%.)

1,5-Di(*p*-isopropylphenyl)thiocarbazone (50)

This was prepared in the same way as (45) starting from the nitroformazan (16). The thiocarbazide was obtained in 91% yield, and the thiocarbazone in 14.2% yield based on the thiocarbazide. The pure (50) melted over the range 142-145°C (decomp.). (Found: C, 67.0; H, 6.5; N, 16.7%. Calc. for $C_{19}H_{23}N_4S$: C, 67.2; H, 6.8; N, 16.5%.)

1,5-Di(*p*-n-butylphenyl)thiocarbazone (51)

The nitroformazan (17) was used to prepare this in exactly the same way as (45) in 27.8% yield based on the thiocarbazide, which was obtained in 89% yield. The pure product (51) melted over the range 118-120°C (decomp.). (Found: C, 68.2; H, 7.3; N, 14.95%. Calc. for $C_{21}H_{27}N_4S$: C, 68.6; H, 7.4; N, 15.2%.)

^{15}N-Labelled dithizone

The 3-nitro-1,5-diphenylformazan labelled at N(1) and N(5) with 96 atom-% ^{15}N (Chapter II) (0.60 g) was suspended in ethanol (15 cm) and treated with ammonia gas and hydrogen sulphide as described for (45) above. Isolation in the same way as (45) gave the ^{15}N-labelled 1,5-diphenylthiocarbazide (0.52 g, 91%). After setting some product aside for n.m.r. spectroscopy, the remainder (0.46 g) was suspended in carbon tetrachloride (300 cm^3) in a 2 litre, two-necked, round-bottomed flask placed in a heating-mantle. A stream of air was bubbled through the solution which was brought to boiling temperature. A long condenser fitted to the flask reduced evaporation of the solvent, but additional portions of solvent were added periodically and the colour of the solution changed to an intense dark green over about 2 hours. Additional solvent (100 cm^3) was added to dissolve some unoxidized thiocarbazide. After a total of 2½ hours of bubbling the carbon tetrachloride was removed on a rotary evaporator. The residue was taken up in the minimum amount of benzene and purified by chromatography as described for (45) above to yield 0.39 g (85.0% based on thiocarbazide) of ^{15}N-labelled dithizone. The use of CCl_4 as solvent in this smooth oxidation of the thiocarbazide was found in trial experiments with unlabelled compounds to give a better yield than diethyl ether (72.3%) or benzene (76.7%), presumably because of the greater

solubility of dithizone in carbon tetrachloride.[5]

Preparation of dithizone *via* 3-chloro-1,5-diphenylformazan (52)

Diethyl malonate (25 g) and sulphuryl chloride (22.8 g) were heated under reflux for 1 hour. Fractionation gave diethyl chloromalonate (b.p. 89-92°C at 4.0-4.2 mm Hg). This chloro-ester (12.5 g) in ethanol (20 cm^3) was treated in the cold with a solution of potassium hydroxide (8.3 g) in ethanol (40 cm^3). Potassium chloromalonate rapidly separated. It was collected and washed well with alcohol, and all traces of solvent were removed by keeping the solid salt under vacuum for several days. Potassium chloromalonate (1.2 g) in water (10 cm^3) containing sodium acetate (3 g) was treated at 0°C (mechanical stirrer) with a diazonium solution prepared in the usual way (Chapter II) from 1.0 g of aniline and 0.80 g of sodium nitrite. A red-orange precipitate slowly formed and after being stirred for 1 hour this was collected and dried. Recrystallization from ethanol gave 3-chloro-1,5-diphenylformazan (52) as an orange microcrystalline powder [0.46 g, 33.0%; m.p. 148-151°C (lit.[186] 150-151°C)].

The conversion of the chloroformazan (52) into dithizone was investigated under two conditions in an attempt to determine a route that would produce the highest yield. Sodium hydrogen sulphide was prepared by dissolving freshly cut sodium metal (0.1 g) in ethanol (40 cm^3) and bubbling hydrogen sulphide gas through the solution. Equal amounts of the chloroformazan (0.23 g) were treated with the NaHS solution in excess (20 cm^3) and one portion was mechanically shaken at room temperature for 15 minutes while the other was gently boiled under reflux for the same time. The resulting red solutions were each added to cold dilute sulphuric acid and the products were isolated as described for (45). The shaking method

gave a yield of 44% compared with 35% for the heating method, both yields being calculated before chromatographic purification. Since the yield of chloroformazan was also small (33%) it was decided not to use this route to synthesize the labelled dithizone, which was consequently synthesized from the nitroformazan as described earlier. The overall yield based on aniline using the chloroformazan route was 14.5% whereas the overall yield on the nitroformazan route was 52.6% (also based on aniline).

^{13}C-Labelled dithizone

This was prepared by a modification of Fischer's original synthesis[1],[187] and the entire reaction sequence was carried out in one and the same vessel. Phenylhydrazine (1.42 g, 0.0132 mol) was dissolved in benzene (20 cm^3) in a 50 cm^3 two-necked flask equipped with a magnetic stirrer and a condenser. Carbon disulphide (91 atom% ^{13}C from BOC Prochem) (0.50 g, 0.0066 mol) was dropped into the solution with stirring, producing a light-yellow, practically solid sludge of the salt (37). The temperature of the flask was raised to 65°C on a water-bath. The precipitate slowly dissolved and H_2S was evolved. After about 20 minutes, when no more H_2S could be detected, the thiocarbazide (38) was presumed to have formed, and a stream of air was drawn through the solution while the temperature was raised to 75°C. Additional benzene (20 cm^3) was added and after 1 hour of bubbling the deep green solution was evaporated to dryness and the crude product was purified chromatographically as described for (45) above to yield the pure ^{13}C-labelled dithizone (0.44 g, 26.1%).

Attempted preparation of 1,5-di(2,6-dimethylphenyl)thiocarbazone

In the first stage 2,6-dimethylphenylhydrazine was prepared. Concentrated

hydrochloric acid (44 cm^3) was cooled to 0°C and 2,6-dimethylaniline (20.60 g) was added over 5 minutes followed by crushed ice (20 g), stirring all the while. The solution was diazotized in the usual way with sodium nitrite (11.7 g) in water (25 cm^3) with vigorous stirring and keeping the temperature below 0°C. A sodium sulphite solution was prepared by dissolving sodium hydroxide pellets (16.7 g) in water (170 cm^3) and adding recrystallized sodium metabisulphite, stirring until all dissolved. After cooling to about 25°C a few drops of phenolphthalein indicator solution was added and small quantities of sodium metabisulphite were introduced until the pink colour just disappeared. A further 4.0 g of sodium metabisulphite were then stirred in. The solution was cooled to about 5°C with stirring and crushed ice (60 g) was added. The ice-cold diazonium solution was run in rapidly with vigorous stirring and the reaction mixture acquired an immediate orange-red colour. The solution was slowly heated to 60-70°C on a water-bath and maintained at this temperature for 45 minutes until the solution was quite dark in colour. The solution was acidified to litmus with concentrated hydrochloric acid (22 cm^3) and heating on the water-bath was continued for 5 hours until the colour was much lighter. Concentrated hydrochloric acid (170 cm^3) was then added to the hot, clear solution, which was cooled in running water and then ice. The hydrochloride of 2,6-dimethylphenylhydrazine separated as pinkish crystals which were filtered off, washed with dilute hydrochloric acid, and pressed dry. The free base was liberated by adding to the hydrochloride salt 40 cm^3 of 25% sodium hydroxide solution. The 2,6-dimethylphenylhydrazine was extracted with two 20 cm^3 portions of toluene. The extracts were dried over 5 g of sodium hydroxide pellets and the toluene removed by distillation. Distillation under reduced pressure yielded the 2,6-dimethylhydrazine

at 146-149°C and 18 mm Hg as an almost colourless liquid (9.5 g, 41%).

The second stage of the synthesis involved reaction of the 2,6-dimethylphenylhydrazine with carbon disulphide in 2 : 1 molar proportion. This was done several times and each time the solid salt $(ArNH{\cdot}NH_3)^+$-$(ArNH{\cdot}NH{\cdot}CS{\cdot}S)^-$ [as (37)] was obtained in good yield. However, when this salt was heated at 98°C with a view to forming the thiocarbazide [as(38)] by loss of hydrogen sulphide, an intractable yellow tar formed, apparently without evolving H_2S. The tar defied all attempts to make it solid and treatment with hot alcoholic potassium hydroxide showed no signs of the characteristic deep red thiocarbazonate anion. The pyrolysis of the initial solid salt was conducted at both lower and higher temperatures than that recommended for dithizone (98°C),[187] also without success.

3-Seleno-1,5-diphenylformazan ('selenazone')

The initial step was the synthesis of aluminium selenide (Al_2Se_3).[202] Aluminium powder (30 g), freed from oil by washing with acetone and ether was thoroughly mixed in a mortar with finely divided selenium powder (50 g). About 5 g of this mixture was placed in a 200 cm^3 heavy walled clay crucible furnished with a well fitting cover. A small piece of magnesium ribbon was ignited, dropped into the crucible and the cover immediately replaced. After a few seconds the cover was again removed and about 3 g of the powdered mixture of aluminium and selenium was added to the glowing mass and the cover was immediately replaced again. Further 3 g portions of the mixture were then added, waiting a few seconds between each addition, and the procedure was repeated until all the mixture had been added. When cold the reaction product was removed

from the crucible and stored in a tightly stoppered container until it was required.

Hydrogen selenide, liberated by dropping water onto aluminium selenide (20 g),[203] was transferred by a stream of dry nitrogen gas into a solution of 3-nitro-1,5-diphenylformazan [(9); 7 g] in ethanol (250 cm^3) which had been saturated with dry ammonia gas at 0°C. Moisture and oxygen were carefully excluded by passing the hydrogen selenide through tubes containing calcium chloride and phosphorus pentoxide and by maintaining a steady stream of dry nitrogen throughout the entire preparation. After 15 minutes the solution was filtered and the solid product washed with water and dried *in vacuo*. The crude selenocarbazide was added to a solution of potassium hydroxide (2 g) in methanol (50 ml) which had previously been brought to its boiling point. After having been boiled under reflux for 5 minutes the solution was poured with constant stirring into 1 *M* sulphuric acid (500 cm^3) cooled at 0°C. Selenazone separated as a black powder and was collected, washed free from acid with water and dried *in vacuo* (1.9 g, 24.1%).

For purification a sample was dissolved in pure chloroform and shaken in a separatory funnel with 1 : 100 aqueous ammonia prepared from isopiestically pure ammonia.[204] The aqueous extract was washed with several successive portions of chloroform which were rejected. Pure chloroform was then added and the selenazone was back-extracted into the organic phase by acidifying the acqueous phase with isopiestic hydrochloric acid.[204] After removal of the solvent *in vacuo*, selenazone was obtained as an odourless microcrystalline black powder which was easily oxidized on standing in the air [m.p. 112-115°C decomp. (lit.[35] 116°C)].

(Found: C, 51.1; H, 4.4; N, 18.6%. Calc. for $C_{13}H_{12}N_4Se$: C, 51.5; H, 4.0; N, 18.5%.)

Dimethylselenide, CH_3SeCH_3

Dimethylselenide was prepared from the reaction of CH_3I and Na_2Se in aqueous base. The Na_2Se was generated *in situ* by reducing powdered Se metal in aqueous sodium hydroxide with sodium formaldehyde sulphoxylate.[188]

A mixture of sodium formaldehyde sulphoxylate ('rongalite'; $CH_3NaO_3S \cdot xH_2O$) (90 g; 0.76 mol), sodium hydroxide (70 g; 1.75 mol), powdered selenium (25 g; 0.32 mol) and freshly distilled water (300 cm^3) was warmed to about 50°C under nitrogen. White needles of air-sensitive sodium selenide separated. Methyl iodide (41.5 cm^3; 0.32 mol) was added slowly. The reaction was vigorous and was completed by warming under reflux for 1 hour. Dimethylselenide was removed by distillation on the water-bath. Distillation over anhydrous sodium sulphate yielded the pure product [29.7 g, 85.0%; b.p. 55-58°C (lit.[188] 57°C)] which was stored over molecular sieves and under nitrogen.

Slow addition of the methyl iodide is essential if the yield of selenide is not to be diminished owing to the formation of trimethylselenonium iodide, which separates on the sides of the flask. Dimethylselenide has a penetrating, sickening odour; the preparation should be conducted in a well-ventilated fume-cupboard.

CHAPTER V

PHOTOCHROMISM IN MERCURY DITHIZONATES

CHAPTER V

PHOTOCHROMISM IN MERCURY DITHIZONATES

1. Introduction

Irradiation by visible light of solutions of mercury(II) bis(dithizonate) [$Hg(HDz)_2$; (5a)] in organic solvents induces a colour change from yellow to blue. The background to this intriguing photochromic reaction was given in Chapter I (*q.v.*). Meriwether, Breitner, and Sloan[40] found this reversible photochromism to be a general reaction of all primary metal dithizonates, but the reverse reaction is generally too rapid to allow visual observation of a colour change. None of the secondary dithizonates (*i.e.*, complexes with both protons removed from the ligand) were found to be photochromic in solution. Of 24 primary dithizonates examined at room temperature and at -80°C, in 16 solvents, 9 were found to be visibly photochromic under test conditions with visible light. Independent of the metal, the colour change was usually from yellow-orange to blue or violet, indicating the primary importance of the ligand, whereas the rate of return to the normal colour depended enormously on the metal, with half-lives varying from about 30 seconds for the mercury complex at 25°C to less than 1 second for cadmium or lead dithizonates, even when cooled to -80°C.

At high levels of illumination at 25°C a steady state could be reached, with 80 - 90% of a solution of mercury(II) dithizonate (5) in benzene in the activated blue form. Under comparable conditions the steady-state concentration for the lead or cadmium complex was only about 0.1%. The strongest photochromic effects were found with dry, non-polar solvents

such as benzene, toluene, carbon tetrachloride, or chloroform, and hydroxylic solvents were notable for their effect in accelerating the back-reaction. One drop of ethanol added to a solution of $Hg(HDz)_2$ in toluene reduced the half-life from 30 seconds at 25°C to less than 1 second at 0°C.[40]

Light of wavelength greater than 450 nm activated all the photochromic dithizonates, but if the wavelength was longer than 640 nm only those of Pd and Pt were activated, showing that activation could occur in more than one of the visible absorption bands [$Pd(HDz)_2$ and $Pt(HDz)_2$ have bands at 450 and 640, and 488 and 710 nm, respectively]. Electron spin resonance measurements showed that free-radical species were absent in the reaction of the mercury complex, and the photochromic process was assigned ionic character. Deuteriation took place very rapidly on shaking a solution of the mercury complex in benzene with D_2O: it also slowed down the return rate about three-fold. By following changes in the i.r. spectra of solutions in CCl_4 during irradiation by white light, the shift of the N-H stretching mode to higher frequencies in the activated blue form indicated the formation of a weaker hydrogen bond. The return rate was studied spectrophotometrically by observing the replacement of the band due to the activated form (ε = 3900 m^2 mol^{-1} at 605 nm) by that of the normal form (ε = 7000 m^2 mol^{-1} at 490 nm) in the mercury complex. Pseudo-first-order kinetics were observed, but the rate was found to be a function of (i) the total concentration of the complex, (ii) the water content, and (iii), in solutions allowed to stand in contact with water, the time that has elapsed since the preparation of the solution.[40,41] Figure 28 shows the visible spectra of the return reaction from the activated form of $Hg(HDz)_2$ as determined in the present work.

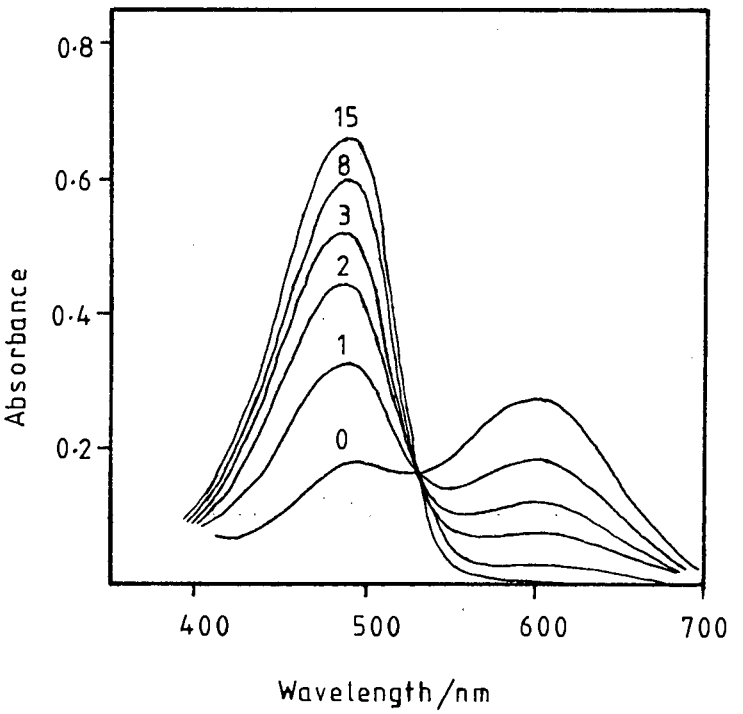


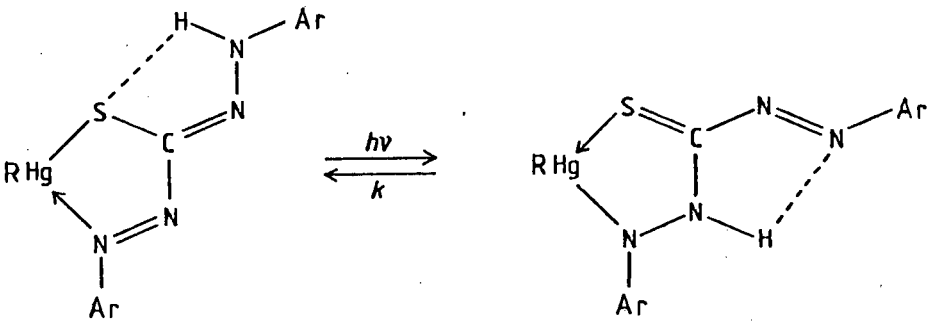
FIGURE 28 : Visible spectra of return reaction of 9.5×10^{-6} *M* $Hg(HDz)_2$ (5) after irradiation in dry chloroform at 20°C. The number on each curve indicates the time in minutes after irradiation.

These results led Meriwether, Breitner, and Colthup[41] to eliminate a number of possible structures for the activated complex, and their preferred reaction scheme is (5a) $\rightleftharpoons$ (5b) (Table 34). Note that the structure (5a) proposed for the primary mercury(II) dithizonate in solution is the same as that found for the solid (Figure 2) save that a strong hydrogen bond is proposed between N(5) and the adjacent sulphur atom instead of to the nitrogen of the pyridine that occurs in the crystalline adduct $Hg(HDz)_2 \cdot 2py$.[42]

The synthesis and study of the organomercury(II) dithizonates reported in the present work was directed towards the further elucidation of the intriguing photochromic reaction of mercury(II) dithizonate, and, by extension, of the primary metal dithizonates in general. In particular, it was of interest to obtain reliable i.r. and n.m.r. data which might substantiate Meriwether's proposed structure for the activated blue form of $Hg(HDz)_2$, *viz* (5b). The complexes (5) and (55) - (60) (Table 34) were prepared by established routes[40,70,205] (see Experimental Section). All these compounds display similar photochromism (yellow $\rightleftharpoons$ blue) when suitably irradiated in organic solvents, with forward and back reactions proceeding at conveniently measurable rates. Moreover, whereas the low concentration (*ca.* 10^{-3} *M*) of even a saturated solution of $Hg(HDz)_2$ in CCl_4[206] restricts reliable measurements by i.r. and n.m.r. spectroscopy, the newly prepared complexes with a single chelated ligand are fully 100-times more soluble.

It has not proved possible to isolate a specimen of the blue isomer of any of the mercury complexes by irradiating crystals of the stable yellow form: photo-isomerization does not appear to proceed at a measurable rate

TABLE 34 : MERCURY(II) AND ORGANOMERCURY(II) COMPLEXES OF DITHIZONE AND SUBSTITUTED DITHIZONES SYNTHESIZED IN THIS WORK



(a) yellow (b) blue

(5)	$Hg(HDz)_2$	:	Ar = Ph;	R = HDz
(55)	PhHg(HDz)	:	Ar = Ph;	R = Ph
(56)	(2,6-diMePh)Hg(HDz)	:	Ar = Ph;	R = 2,6-dimethylphenyl
(57)	(2,4,6-triMePh)Hg(HDz)	:	Ar = Ph;	R = 2,4,6-trimethylphenyl
(58)	MeHg(HDz)	:	Ar = Ph;	R = Me
(59)	MeHg(*p*-tolyl-HDz)	:	Ar = *p*-tolyl;	R = Me
(60)	MeHg(*o*-tolyl-HDz)	:	Ar = *o*-tolyl;	R = Me

in the absence of a solvent. Nor has it proved possible to secure crystals of the blue form by carefully and slowly concentrating a solution kept in the blue form by constant and intense illumination: only the stable yellow form crystallizes out. Thus, whereas the structure of phenylmercury(II) dithizonate [PhHg(HDz); (55)] has been established unambiguously in the present work by *X*-ray crystallography, it has only been possible to assign the structure of the blue isomer from measurements on irradiated solutions. Since dithizone is a bidentate chelating agent the interesting possibility of three-coordination about the mercury atom arises in these 1 : 1 dithizonates derived from organomercury(II), and the structure of methylmercury(II) dithizonate [MeHg(HDz); (58)] was also determined by *X*-ray crystallography because it was thought that the phenyl group on the mercury atom in (55) might be hindering approach of the donor nitrogen atom N(1) of the dithizonate ligand towards the central mercury atom.

2. Crystal and molecular structures of phenyl- and methylmercury(II) dithizonate

The instruments and experimental methods used in this study were the same as those used and described in Chapter II, and they will not be repeated here unless necessary.

Crystal and intensity data

PhHg(HDz) (55) and MeHg(HDz) (58) were prepared as described in the Experimental Section of this Chapter. Fragile red-brown needles of PhHg(HDz) were elongated along a and were obtained by slow evaporation at room temperature from benzene/n-butanol. Needles of MeHg(HDz), obtained similarly, were elongated along c. Microanalysis and m.p. data are given in Table 35.

Preliminary cell dimensions and space-group symmetry were determined from oscillation and Weissenberg photographs. For (55) the systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ indicated the space group $P2_1/c$. No systematic absences were found for (58); the space group $P\bar{1}$ was chosen from analysis of E-statistics and confirmed by successful refinement of the structure. Accurate lattice constants were obtained by least-squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). During the collection of intensity data three reference reflections were periodically monitored to check crystal stability. The data were corrected for Lorentz-polarization effects but not for absorption. Crystal data and experimental details are listed in Table 35.

TABLE 55 : CRYSTAL DATA AND EXPERIMENTAL AND REFINEMENT PARAMETERS FOR THE CRYSTAL STRUCTURES OF PHENYLMERCURY(II) DITHIZONATE (55) AND METHYLMERCURY(II) DITHIZONATE (58)

	Compound (55)	Compound (58)
Crystal data		
Molecular formula	$(C_6H_5)Hg(C_{13}H_{11}N_4S)$	$(CH_3)Hg(C_{13}H_{11}N_4S)$
M_r	533.03	470.96
Space group	$P2_1/c$	$P\bar{1}$
a/Å	5.991(3)	14.866(7)
b/Å	20.68(1)	11.194(6)
c/Å	17.129(9)	4.557(3)
α/°		89.30(5)
β/°	99.40(5)	95.85(5)
γ/°		97.62(5)
V/Å^3	2094(2)	748(1)
D_m/Mg m^{-3}	1.63	2.01
D_c/Mg m^{-3}	1.69 for Z = 4	2.09 for Z = 2
μ(Mo-K_α)/cm^{-1}	7.17	10.0
F(000)	1016	444
Melting point/°C	172-173 decomp.	152-155 decomp.
Composition		
%C Found (Calc.)	42.25 (42.8)	35.9 (35.7)
%H	3.1 (3.0)	3.0 (3.0)
%N	10.45 (10.5)	11.85 (11.9)
Data collection		
Crystal dimensions/mm	0.50 × 0.04 × 0.02	0.70 × 0.05 × 0.15
Scan mode	ω - 2θ	ω - 2θ
Scan width/°θ	1.2	1.2
Scan speed/°θs^{-1}	0.04	0.04
Range scanned (2θ)/°	6 - 40	6 - 46
Stability of standard reflections/%	1.3	1.5
Number of reflections collected	2029	2062
Number of observed reflections	1354 with I(rel)>2σI(rel)	1836 with I(rel) >2σI(rel)
Refinement		
Number of variables	117	106
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.058	0.061
$R_w = \sum w^{\frac{1}{2}}\|\|F_o\| - \|F_c\|\|/\sum w^{\frac{1}{2}}\|F_o\|$	0.060	0.058
Weighting scheme w	$(\sigma^2 F_o + 0.0018F_o^2)^{-1}$	$(\sigma^2 F_o)^{-1}$
U_{iso} of H atoms in calculated positions/Å		
Aromatic H	0.08(2)	0.08(2)
Methyl H	-	0.10(4)
U_{iso} of constrained imino H(N5)/Å^2	0.05(7)	0.03(4)

Solution and refinement of the structures

Both structures were solved by locating the Hg atoms in Patterson maps; subsequent weighted difference syntheses yielded the positions of all the remaining non-hydrogen atoms and several peaks were found in chemically reasonable positions for H atoms. The final full-matrix least-squares refinement was carried out with the Hg and S atoms treated anisotropically and the remaining non-hydrogen atoms isotropically. The aromatic H atoms were constrained to ride at 1.08 Å from their respective parent C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as a single parameter. The methyl H atoms in (58) were similarly placed in calculated positions and refined as a rigid group with a single temperature factor. In both structures the imino proton, H(N5), which had been revealed in previous difference electron density maps, was fixed at 1.00 ± 0.01 Å from N(5) and its temperature factor was refined independently. Details of the final refinements are given in Table 35. The weighting schemes were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by analyses of variance computed after the final cycles (Tables 36 and 37). In the final cycle for each structure the mean e.s.d. in the parameters of the non-hydrogen atoms was greater than 100 times the average parameter shift, while final difference maps were smooth except close to Hg where the largest residual peaks were 1.0 (55) and 2.2 eÅ^{-3} (58). Complex neutral-atom scattering factors were taken from Cromer and Mann[109] for Hg, C, N, and S, and from Stewart, Davidson, and Simpson[110] for H, with anomalous dispersion corrections from Cromer and Liberman.[111] Tables 38 and 39 list the observed and calculated structure factors, while

TABLE 36 : ANALYSIS OF VARIANCE[a] FOR PHENYLMERCURY(II) DITHIZONATE (55)

(a) As a function of sin θ

sin θ	0.00 - 0.15	0.19	0.22	0.25	0.27	0.29	0.30	0.32	0.33 - 0.35
N	145	142	149	164	143	139	88	193	90	101
V	1292	517	468	472	417	467	421	560	615	597

(b) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.31	0.35	0.37	0.40	0.44	0.48	0.51	0.55	0.63 - 1.00
N	150	170	87	135	151	142	125	129	130	135
V	976	582	567	702	559	489	541	421	748	557

(c) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	181	207	186	177	149	145	152	157	1354
V	658	692	526	556	601	514	733	770	638

(d) As a function of |Miller index|

|*h*|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	186	348	313	257	169	81	0	0	0	0	0	0	0	0	0
V	848	746	537	515	495	536	0	0	0	0	0	0	0	0	0

|*k*|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	60	116	111	89	109	112	73	98	103	62	79	76	48	63	155
V	757	718	737	945	784	599	575	561	461	552	511	487	497	530	541

|*l*|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	70	106	138	112	136	104	117	89	113	80	78	57	58	39	57
V	1023	1039	713	617	528	550	487	499	531	522	493	504	453	594	558

[a] N = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections.

TABLE 37 : ANALYSIS OF VARIANCE[a] FOR METHYLMERCURY(II) DITHIZONATE (58)

(a) As a function of sin θ

sin θ	0.00 - 0.18	0.18 - 0.23	0.23 - 0.26	0.26 - 0.28	0.28 - 0.31	0.31 - 0.33	0.33 - 0.35	0.35 - 0.36	0.36 - 0.38	0.38 - 0.40
N	199	203	187	145	229	206	198	118	214	137
V	608	393	349	276	234	222	209	195	187	183

(b) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.23	0.23 - 0.27	0.27 - 0.30	0.30 - 0.33	0.33 - 0.36	0.36 - 0.39	0.39 - 0.43	0.43 - 0.47	0.47 - 0.54	0.54 - 1.00
N	197	186	176	211	194	159	198	161	179	175
V	148	180	202	227	258	290	277	385	441	577

(c) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	240	236	237	229	225	215	219	235	1836
V	328	332	283	300	332	375	316	281	319

(d) As a function of |Miller index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	82	166	168	164	156	159	148	136	133	114	109	91	78	62	70
V	394	383	384	402	354	341	336	320	233	184	190	182	216	232	263
$\|k\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	111	218	217	215	206	189	176	151	126	102	69	45	11	0	0
V	650	400	320	307	314	261	240	192	165	175	200	263	326	0	0
$\|l\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	Rest
N	278	542	477	350	187	2	0	0	0	0	0	0	0	0	0
V	355	355	317	280	213	18	0	0	0	0	0	0	0	0	0

[a] *N* = No. of reflections in the group

$V = 100[M\Sigma(\omega|F_o - F_c|^2)/N\Sigma\omega]$

M = total no. of reflections.

TABLE 38 : OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (55)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	140	96	0	8	0	128	-124	1	18	0	38	-30	-5	5	1	88	87	2	9	1	57	49
2	0	0	190	-169	1	8	0	75	-80	2	18	0	66	66	-3	5	1	174	-163	-4	10	1	89	86
3	0	0	152	-138	2	8	0	33	32	-5	1	1	66	-62	-2	5	1	88	-86	-3	10	1	63	61
5	0	0	70	67	3	8	0	79	73	-3	1	1	145	134	-1	5	1	78	70	-2	10	1	124	-124
1	1	0	183	166	5	8	0	43	-39	-2	1	1	173	173	0	5	1	192	162	-1	10	1	210	-202
2	1	0	84	78	1	9	0	215	-203	-1	1	1	84	-102	1	5	1	225	183	1	10	1	167	155
4	1	0	62	-67	2	9	0	102	-100	1	1	1	54	-85	2	5	1	143	-131	2	10	1	48	44
1	2	0	33	-9	3	9	0	74	72	2	1	1	180	171	3	5	1	146	-136	3	10	1	57	-43
2	2	0	123	-112	4	9	0	106	98	3	1	1	114	118	4	5	1	43	31	4	10	1	97	-95
3	2	0	50	-42	5	9	0	32	33	5	1	1	79	-77	5	5	1	88	91	-3	11	1	102	100
5	2	0	48	41	0	10	0	110	112	-5	2	1	54	-50	-2	6	1	40	-30	-2	11	1	90	91
1	3	0	208	189	2	10	0	48	-42	-4	2	1	169	-155	-1	6	1	23	-16	-1	11	1	49	-45
2	3	0	199	177	3	10	0	61	-58	-3	2	1	49	-50	2	6	1	40	-38	0	11	1	189	-183
3	3	0	27	-28	1	11	0	106	-106	-2	2	1	172	163	-5	7	1	66	64	1	11	1	44	-43
4	3	0	172	-161	2	11	0	59	-53	-1	2	1	163	150	-3	7	1	154	-148	2	11	1	111	101
5	3	0	41	-40	4	11	0	67	60	1	2	1	165	-154	-2	7	1	86	-89	3	11	1	96	91
0	4	0	111	-147	0	12	0	208	201	2	2	1	147	-139	-1	7	1	91	86	-3	12	1	32	22
1	4	0	31	9	1	12	0	79	74	3	2	1	83	77	0	7	1	222	200	1	12	1	30	29
2	4	0	51	45	2	12	0	109	-106	4	2	1	100	100	1	7	1	63	50	3	12	1	29	27
3	4	0	135	127	3	12	0	122	-116	-3	3	1	54	-50	2	7	1	134	-129	-4	13	1	28	17
5	4	0	60	-49	1	13	0	32	34	-1	3	1	96	-102	3	7	1	141	-138	-3	13	1	90	85
1	5	0	49	46	2	13	0	55	55	0	3	1	18	-55	5	7	1	94	85	-2	13	1	81	76
2	5	0	106	107	4	13	0	51	-42	1	3	1	133	102	-5	8	1	44	35	-1	13	1	64	-63
3	5	0	59	-53	0	14	0	76	69	3	3	1	48	-42	-4	8	1	84	78	0	13	1	150	-149
4	5	0	85	-84	2	14	0	55	-56	-5	4	1	40	-31	-3	8	1	78	79	1	13	1	44	-44
0	6	0	182	-190	3	14	0	39	-40	-4	4	1	129	-119	-2	8	1	118	-118	2	13	1	90	84
1	6	0	54	-65	1	15	0	106	100	-3	4	1	35	-36	-1	8	1	183	-183	3	13	1	90	95
2	6	0	152	131	2	15	0	98	100	-2	4	1	199	175	0	8	1	50	51	-4	14	1	77	-75
3	6	0	180	173	0	16	0	57	-52	-1	4	1	97	90	1	8	1	233	222	-2	14	1	95	97
5	6	0	106	-100	2	16	0	53	53	0	4	1	38	-30	2	8	1	41	34	-1	14	1	65	67
1	7	0	138	-128	3	16	0	44	34	1	4	1	362	-330	3	8	1	65	-65	1	14	1	88	-88
3	7	0	48	46	1	17	0	44	42	2	4	1	156	-146	4	8	1	85	-79	2	14	1	78	-72
4	7	0	52	46	2	17	0	48	54	3	4	1	53	53	5	8	1	34	-20	-2	16	1	80	81
5	7	0	34	16	0	18	0	95	-92	4	4	1	124	124	1	9	1	39	33	-1	16	1	75	74

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	16	1	100	-102	-3	3	2	74	65	3	6	2	153	145	3	10	2	40	-36	1	17	2	54	56
2	16	1	87	-79	-2	3	2	201	-194	4	6	2	38	-45	-4	11	2	48	-43	2	17	2	53	58
-2	17	1	66	-61	-1	3	2	185	-173	5	6	2	95	-101	-3	11	2	43	-41	-2	18	2	40	42
0	17	1	91	93	0	3	2	129	144	-4	7	2	41	-42	-2	11	2	78	76	-1	18	2	43	-45
2	17	1	59	-66	1	3	2	297	310	-3	7	2	27	-27	-1	11	2	106	109	0	18	2	97	-95
0	19	1	80	80	2	3	2	122	122	-2	7	2	124	120	0	11	2	31	-30	2	18	2	77	77
-5	0	2	63	62	3	3	2	101	-100	-1	7	2	124	122	1	11	2	115	-104	-1	19	2	40	38
-3	0	2	137	-131	4	3	2	116	-114	1	7	2	84	-74	-3	12	2	106	-103	1	19	2	41	-41
-2	0	2	217	-203	-5	4	2	56	-56	2	7	2	31	-26	-2	12	2	85	-90	-5	1	3	55	-55
-1	0	2	250	236	-3	4	2	76	75	3	7	2	35	39	-1	12	2	93	89	-4	1	3	47	38
1	0	2	91	68	-2	4	2	79	76	4	7	2	65	60	0	12	2	178	175	-3	1	3	166	163
2	0	2	228	-225	-1	4	2	92	-92	-5	8	2	46	-43	1	12	2	40	37	-2	1	3	139	141
3	0	2	164	-166	0	4	2	40	-54	-3	8	2	108	110	2	12	2	124	-117	-1	1	3	157	-154
5	0	2	99	103	1	4	2	111	-133	-1	8	2	48	-55	3	12	2	100	-93	0	1	3	147	-146
-5	1	2	38	35	2	4	2	82	80	0	8	2	115	-122	-4	13	2	55	55	1	1	3	23	5
-4	1	2	70	69	3	4	2	80	75	1	8	2	76	-76	-2	13	2	59	-62	2	1	3	144	138
-3	1	2	42	45	5	4	2	49	-37	2	8	2	99	95	-1	13	2	36	-39	3	1	3	114	114
-2	1	2	73	-73	-5	5	2	31	34	3	8	2	91	84	1	13	2	58	56	5	1	3	84	-89
-1	1	2	191	-183	-4	5	2	62	67	5	8	2	35	-38	2	13	2	55	54	-5	2	3	64	-64
1	1	2	104	104	-2	5	2	43	-40	-5	9	2	54	-52	3	13	2	44	-44	-4	2	3	126	-123
2	1	2	89	87	-1	5	2	99	-99	-4	9	2	96	-97	4	13	2	45	-44	-3	2	3	27	-26
3	1	2	60	-62	0	5	2	109	-88	-3	9	2	48	-50	-3	14	2	62	-58	-2	2	3	189	181
4	1	2	53	-52	1	5	2	187	199	-2	9	2	163	156	-2	14	2	43	-45	-1	2	3	267	262
-5	2	2	53	51	2	5	2	98	99	-1	9	2	200	194	0	14	2	89	84	0	2	3	24	-16
-3	2	2	114	-107	3	5	2	52	-55	0	9	2	79	-71	2	14	2	53	-48	1	2	3	291	-284
-2	2	2	134	-118	4	5	2	74	-75	1	9	2	234	-225	-3	15	2	30	20	2	2	3	102	-101
-1	2	2	144	131	-5	6	2	86	-89	2	9	2	95	-85	-2	15	2	94	-97	3	2	3	82	87
0	2	2	128	91	-4	6	2	35	32	3	9	2	70	62	-1	15	2	83	-84	4	2	3	89	100
1	2	2	20	-38	-3	6	2	187	183	4	9	2	92	90	1	15	2	132	126	-3	3	3	24	30
2	2	2	39	-43	-2	6	2	108	109	-3	10	2	51	-46	2	15	2	59	60	-2	3	3	61	66
3	2	2	47	-48	-1	6	2	96	-95	-2	10	2	61	-53	3	15	2	58	-60	0	3	3	65	51
5	2	2	46	48	0	6	2	171	-177	-1	10	2	49	53	-2	16	2	34	32	1	3	3	133	121
-5	3	2	59	61	1	6	2	134	-147	0	10	2	96	88	0	16	2	54	-54	2	3	3	24	-25
-4	3	2	149	144	2	6	2	165	156	2	10	2	75	-77	2	16	2	31	35	-5	4	3	46	-46

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	4	3	114	-115	-2	8	3	121	-122	-4	14	3	78	-86	2	1	4	62	62	1	5	4	69	80
-3	4	3	37	-41	-1	8	3	146	-147	-2	14	3	92	91	3	1	4	41	-38	2	5	4	78	81
-2	4	3	126	114	0	8	3	84	80	-1	14	3	94	88	4	1	4	65	-62	3	5	4	60	-63
-1	4	3	161	150	1	8	3	176	177	1	14	3	117	-116	-3	2	4	117	-111	4	5	4	73	-65
0	4	3	120	-110	2	8	3	85	85	2	14	3	73	-73	-2	2	4	109	-98	-5	6	4	78	-75
1	4	3	242	-232	3	8	3	55	-54	3	14	3	91	91	-1	2	4	124	125	-4	6	4	55	55
2	4	3	114	-103	4	8	3	89	-90	-2	16	3	44	46	0	2	4	196	209	-3	6	4	143	142
3	4	3	107	105	-3	9	3	42	-37	-1	16	3	54	62	1	2	4	34	-32	-2	6	4	63	64
4	4	3	111	114	1	9	3	85	77	1	16	3	103	-99	2	2	4	54	-57	-1	6	4	106	-102
-5	5	3	84	78	2	9	3	31	-40	2	16	3	69	-66	3	2	4	59	-56	0	6	4	238	-243
-4	5	3	40	-47	-4	10	3	79	83	3	16	3	77	78	5	2	4	42	47	2	6	4	207	203
-3	5	3	160	-148	-3	10	3	30	24	-2	17	3	42	-40	-5	3	4	56	50	3	6	4	105	107
-2	5	3	94	-90	-2	10	3	135	-135	-1	17	3	53	50	-4	3	4	144	140	4	6	4	56	-52
-1	5	3	94	95	-1	10	3	141	-159	0	17	3	71	75	-2	3	4	217	-213	5	6	4	55	-47
0	5	3	214	199	0	10	3	39	49	2	17	3	71	-63	-1	3	4	230	-230	-4	7	4	49	-43
2	5	3	148	-150	1	10	3	115	124	-2	18	3	31	5	0	3	4	43	53	-2	7	4	60	55
3	5	3	125	-121	2	10	3	90	86	-1	19	3	55	64	1	3	4	201	225	-1	7	4	61	57
4	5	3	32	29	3	10	3	53	-50	0	19	3	70	75	2	3	4	105	105	0	7	4	81	-74
5	5	3	59	59	4	10	3	59	-57	-5	0	4	50	52	3	3	4	124	-124	1	7	4	117	-109
-1	6	3	34	33	-3	11	3	96	97	-4	0	4	43	-43	4	3	4	102	-106	2	7	4	73	-64
2	6	3	51	-41	-2	11	3	98	96	-3	0	4	210	-206	-5	4	4	49	-51	3	7	4	34	38
-5	7	3	80	79	-1	11	3	108	-110	-2	0	4	138	-137	-4	4	4	31	29	4	7	4	46	49
-4	7	3	31	-25	0	11	3	126	-127	-1	0	4	86	83	-3	4	4	107	105	-5	8	4	34	-43
-3	7	3	145	-139	2	11	3	85	82	0	0	4	155	155	-1	4	4	84	-81	-3	8	4	71	72
-2	7	3	87	-84	3	11	3	62	63	1	0	4	48	-49	0	4	4	167	-180	-2	8	4	56	58
-1	7	3	121	115	0	12	3	52	53	2	0	4	166	-162	2	4	4	112	110	-1	8	4	39	-37
0	7	3	186	177	3	12	3	29	22	3	0	4	126	-128	3	4	4	48	45	0	8	4	102	-108
1	7	3	69	67	-3	13	3	90	96	5	0	4	89	90	4	4	4	36	-27	2	8	4	138	130
2	7	3	170	-166	-2	13	3	64	68	-5	1	4	34	40	-5	5	4	33	33	3	8	4	71	66
3	7	3	102	-101	-1	13	3	90	-89	-4	1	4	82	82	-4	5	4	65	63	-4	9	4	107	-105
4	7	3	38	39	0	13	3	118	-120	-2	1	4	116	-110	-3	5	4	40	-35	-2	9	4	127	130
5	7	3	56	56	2	13	3	95	96	-1	1	4	118	-119	-2	5	4	76	-75	-1	9	4	140	143
-4	8	3	92	88	3	13	3	82	79	0	1	4	36	-33	-1	5	4	61	-65	0	9	4	73	-70
-3	8	3	27	24	4	13	3	31	-16	1	1	4	140	146	0	5	4	44	55	1	9	4	171	-161

TABLE 38 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	9	4	80	-75	0	14	4	82	77	3	2	5	90	94	-3	7	5	121	-120	-1	12	5	33	-17
3	9	4	71	71	2	14	4	50	-45	4	2	5	81	83	-2	7	5	68	-65	-3	13	5	90	100
4	9	4	108	107	3	14	4	69	-62	-5	3	5	33	25	-1	7	5	88	87	-2	13	5	54	51
-3	10	4	51	-49	-2	15	4	70	-77	-4	3	5	31	-25	0	7	5	207	202	-1	13	5	68	-61
-2	10	4	32	-30	-1	15	4	102	-102	-3	3	5	24	3	2	7	5	174	-174	0	13	5	126	-123
-1	10	4	75	78	0	15	4	29	31	-2	3	5	25	20	3	7	5	93	-86	2	13	5	88	83
0	10	4	71	74	1	15	4	126	123	-1	3	5	90	-82	4	7	5	42	36	3	13	5	55	53
2	10	4	60	-59	2	15	4	61	58	0	3	5	29	-26	-5	8	5	34	30	-2	14	5	78	75
3	10	4	49	-39	3	15	4	70	-75	4	3	5	31	19	-4	8	5	87	85	-1	14	5	92	91
4	10	4	36	31	-3	16	4	39	43	-5	4	5	48	-52	-2	8	5	166	-159	0	14	5	36	-28
-4	11	4	49	-51	-1	16	4	42	-42	-4	4	5	104	-107	-1	8	5	95	-94	1	14	5	127	-125
-2	11	4	100	100	0	16	4	46	-47	-2	4	5	192	186	0	8	5	92	93	3	14	5	49	53
-1	11	4	89	88	-2	17	4	30	-36	-1	4	5	123	120	1	8	5	112	121	-2	16	5	66	71
0	11	4	70	-66	-1	17	4	52	-43	0	4	5	87	-88	2	8	5	43	53	-1	16	5	66	63
1	11	4	56	-55	1	17	4	63	60	1	4	5	144	-140	3	8	5	69	-69	0	16	5	34	-22
2	11	4	49	-44	-2	18	4	49	43	2	4	5	62	-60	4	8	5	106	-106	1	16	5	107	-104
4	11	4	47	52	-1	18	4	79	-74	3	4	5	112	109	-1	9	5	33	-31	-1	17	5	61	60
-3	12	4	129	-126	0	18	4	91	-88	4	4	5	92	90	-4	10	5	94	93	0	17	5	75	75
-2	12	4	78	-75	-5	1	5	54	-49	-5	5	5	58	60	-3	10	5	36	28	2	17	5	63	-56
-1	12	4	109	111	-3	1	5	173	173	-4	5	5	54	-52	-2	10	5	150	-148	-1	18	5	34	20
0	12	4	140	135	-2	1	5	91	93	-3	5	5	148	-146	-1	10	5	99	-101	-5	0	6	98	96
2	12	4	81	-83	-1	1	5	154	-150	-2	5	5	32	-27	0	10	5	62	55	-3	0	6	202	-199
3	12	4	84	-82	0	1	5	221	-218	-1	5	5	117	122	1	10	5	140	145	-2	0	6	52	-51
4	12	4	32	21	2	1	5	113	115	0	5	5	197	206	2	10	5	40	36	-1	0	6	278	271
-4	13	4	53	50	3	1	5	114	112	1	5	5	34	-31	3	10	5	41	-32	0	0	6	147	159
-3	13	4	29	-13	4	1	5	30	-40	2	5	5	187	-188	4	10	5	88	-86	2	0	6	103	-99
-2	13	4	39	-43	5	1	5	64	-74	3	5	5	77	-75	-4	11	5	31	24	3	0	6	109	-109
-1	13	4	60	-62	-5	2	5	45	-44	4	5	5	45	50	-3	11	5	114	113	4	0	6	60	58
1	13	4	69	69	-4	2	5	113	-114	-3	6	5	45	45	-2	11	5	28	32	-5	1	6	32	34
3	13	4	54	-48	-3	2	5	32	23	-2	6	5	54	48	-1	11	5	107	-104	-4	1	6	46	46
-4	14	4	33	-14	-2	2	5	161	160	0	6	5	47	56	0	11	5	128	-128	-2	1	6	101	-98
-3	14	4	58	-59	-1	2	5	199	192	1	6	5	58	-49	2	11	5	110	105	-1	1	6	29	-27
-2	14	4	41	-48	1	2	5	185	-182	-5	7	5	50	53	3	11	5	74	75	0	1	6	49	54
-1	14	4	49	49	2	2	5	90	-89	-4	7	5	45	-53	4	11	5	35	-37	1	1	6	92	94

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	1	6	46	-44	-3	6	6	151	143	0	11	6	29	-28	0	18	6	68	-72	-3	5	7	85	-84
4	1	6	42	-48	-2	6	6	53	52	1	11	6	56	-57	-5	1	7	78	-84	-2	5	7	61	-61
-3	2	6	106	-105	-1	6	6	149	-148	3	11	6	57	53	-4	1	7	39	36	-1	5	7	153	154
-2	2	6	36	-29	0	6	6	218	-221	-4	12	6	46	-36	-3	1	7	145	144	0	5	7	178	182
-1	2	6	149	148	2	6	6	190	192	-3	12	6	119	-117	-2	1	7	43	39	2	5	7	144	-147
0	2	6	96	105	3	6	6	74	73	-2	12	6	47	-45	-1	1	7	224	-220	4	5	7	39	31
2	2	6	101	-104	-4	7	6	55	-56	-1	12	6	94	99	0	1	7	111	-112	-2	6	7	30	-30
3	2	6	71	-83	-2	7	6	109	103	0	12	6	122	121	2	1	7	138	144	-5	7	7	51	43
-5	3	6	71	69	0	7	6	79	-89	2	12	6	107	-110	3	1	7	88	83	-4	7	7	67	-63
-4	3	6	92	99	1	7	6	72	-68	3	12	6	48	-53	4	1	7	51	-48	-3	7	7	106	-107
-2	3	6	187	-185	4	7	6	49	53	-2	13	6	39	-36	-5	2	7	75	-88	-2	7	7	28	-21
-1	3	6	181	-184	-5	8	6	43	-39	-1	13	6	35	-38	-4	2	7	60	-56	-1	7	7	110	109
0	3	6	53	53	-4	8	6	33	34	0	13	6	43	36	-2	2	7	152	153	0	7	7	130	137
1	3	6	215	217	-3	8	6	54	50	1	13	6	43	47	-1	2	7	108	108	2	7	7	110	-109
3	3	6	107	-108	-1	8	6	36	-33	3	13	6	31	-23	0	2	7	88	-93	3	7	7	63	-64
4	3	6	90	-93	0	8	6	96	-91	-3	14	6	56	-47	1	2	7	188	-193	-5	8	7	52	47
-4	4	6	49	47	2	8	6	69	64	-1	14	6	42	52	3	2	7	104	102	-4	8	7	94	88
-3	4	6	66	68	3	8	6	42	39	0	14	6	56	57	4	2	7	55	45	-3	8	7	27	-22
-2	4	6	39	37	-4	9	6	93	-97	2	14	6	61	-54	-4	3	7	29	-29	-2	8	7	154	-155
-1	4	6	49	-42	-2	9	6	186	188	3	14	6	49	-39	-3	3	7	26	22	-1	8	7	52	-45
0	4	6	84	-85	-1	9	6	109	109	-2	15	6	87	-80	-2	3	7	63	-59	0	8	7	66	71
1	4	6	36	37	0	9	6	58	-58	-1	15	6	64	-62	-1	3	7	43	-38	1	8	7	110	108
2	4	6	102	108	1	9	6	149	-142	0	15	6	45	47	0	3	7	28	19	3	8	7	78	-78
-5	5	6	52	48	2	9	6	40	-37	1	15	6	117	121	1	3	7	29	-27	4	8	7	56	-60
-4	5	6	43	41	3	9	6	72	74	2	15	6	30	25	-5	4	7	68	-71	4	9	7	31	15
-3	5	6	27	-20	4	9	6	81	85	-3	16	6	43	42	-4	4	7	75	-78	-4	10	7	84	85
-2	5	6	105	-95	-3	10	6	57	-57	-1	16	6	48	-41	-2	4	7	119	123	-2	10	7	150	-150
-1	5	6	63	-64	-1	10	6	54	56	0	16	6	33	-35	-1	4	7	140	143	-1	10	7	92	-95
0	5	6	39	41	0	10	6	77	74	2	16	6	40	40	0	4	7	92	-96	0	10	7	72	73
1	5	6	148	147	2	10	6	67	-71	-2	17	6	56	-50	1	4	7	190	-194	1	10	7	104	103
3	5	6	57	-58	3	10	6	50	-44	-1	17	6	36	-43	3	4	7	86	88	2	10	7	41	45
4	5	6	41	-33	-4	11	6	59	-56	0	17	6	31	16	4	4	7	62	60	3	10	7	87	-82
-5	6	6	47	-51	-2	11	6	101	93	1	17	6	44	47	-5	5	7	37	38	-4	11	7	38	32
-4	6	6	75	68	-1	11	6	67	69	-1	18	6	62	-60	-4	5	7	56	-59	-3	11	7	95	94

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	11	7	36	36	-1	1	8	37	-35	-1	5	8	93	-90	2	9	8	35	-44	-3	1	9	136	139
-1	11	7	101	-100	0	1	8	52	56	0	5	8	82	83	3	9	8	89	90	-2	1	9	27	-22
0	11	7	83	-82	1	1	8	64	65	1	5	8	91	91	-3	10	8	58	-64	-1	1	9	108	-96
2	11	7	95	90	3	1	8	63	-64	3	5	8	54	-51	-1	10	8	54	50	0	1	9	104	-107
3	11	7	52	39	4	1	8	36	-31	4	5	8	32	-38	2	10	8	49	-36	1	1	9	37	36
-3	13	7	97	93	-5	2	8	43	45	-5	6	8	31	-28	-4	11	8	67	-56	2	1	9	111	108
-2	13	7	37	34	-4	2	8	31	-33	-4	6	8	41	65	-2	11	8	70	68	3	1	9	35	38
-1	13	7	99	-102	-3	2	8	79	-77	-3	6	8	106	100	0	11	8	28	-27	4	1	9	60	-62
0	13	7	90	-94	-1	2	8	82	84	-2	6	8	33	27	1	11	8	55	-53	-5	2	9	42	-49
2	13	7	92	88	0	2	8	48	46	-1	6	8	187	-183	2	11	8	39	-36	-4	2	9	95	-96
3	13	7	45	46	2	2	8	85	-79	0	6	8	201	-206	3	11	8	32	34	-2	2	9	149	144
-2	14	7	47	48	3	2	8	45	-50	1	6	8	46	45	-4	12	8	31	-33	-1	2	9	37	34
-1	14	7	51	56	4	2	8	43	37	2	6	8	131	130	-3	12	8	101	-100	0	2	9	136	-133
0	14	7	55	-53	-5	3	8	87	85	3	6	8	51	55	-2	12	8	44	-48	1	2	9	117	-118
1	14	7	98	-92	-4	3	8	101	101	4	6	8	42	-41	-1	12	8	113	119	3	2	9	79	82
2	14	7	33	-11	-3	3	8	40	-35	-4	7	8	57	-57	0	12	8	90	87	4	2	9	64	59
-2	16	7	67	68	-2	3	8	146	-143	-3	7	8	58	56	1	12	8	30	-26	-5	3	9	37	-18
-1	16	7	64	62	-1	3	8	111	-108	-2	7	8	85	93	2	12	8	103	-102	-4	3	9	43	43
0	16	7	40	-39	0	3	8	136	138	-1	7	8	44	45	3	12	8	38	-35	-5	4	9	69	-65
1	16	7	104	-95	1	3	8	178	182	0	7	8	38	-42	-3	13	8	31	-1	-4	4	9	85	-84
-1	17	7	61	70	2	3	8	33	38	1	7	8	62	-68	-1	13	8	33	-33	-2	4	9	154	148
0	17	7	60	56	3	3	8	106	-108	3	7	8	56	60	0	13	8	43	42	-1	4	9	103	99
-5	0	8	83	88	4	3	8	74	-71	-4	8	8	29	28	1	13	8	60	61	0	4	9	94	-94
-4	0	8	60	-67	-5	4	8	28	-12	-3	8	8	46	50	-3	14	8	42	-46	1	4	9	145	-147
-3	0	8	193	-196	-4	4	8	29	24	-2	8	8	36	33	-1	14	8	70	67	3	4	9	84	84
-2	0	8	27	-13	-3	4	8	38	33	-1	8	8	68	-61	0	14	8	50	50	4	4	9	58	56
-1	0	8	139	141	-2	4	8	44	45	0	8	8	83	-81	2	14	8	45	-42	-4	5	9	41	-41
0	0	8	141	142	-1	4	8	41	-40	2	8	8	64	59	-2	15	8	70	-70	-3	5	9	90	-90
2	0	8	139	-138	0	4	8	105	-104	-4	9	8	89	-90	-1	15	8	65	-70	-2	5	9	44	-38
3	0	8	70	-65	2	4	8	53	60	-3	9	8	51	47	0	15	8	44	48	-1	5	9	123	118
4	0	8	77	76	-5	5	8	33	30	-2	9	8	150	150	1	15	8	92	86	0	5	9	140	140
-5	1	8	42	47	-4	5	8	37	41	-1	9	8	61	56	-1	16	8	48	-38	1	5	9	73	-71
-4	1	8	56	58	-3	5	8	26	6	0	9	8	107	-108	-1	17	8	41	-44	2	5	9	109	-105
-2	1	8	85	-81	-2	5	8	82	-78	1	9	8	123	-125	-4	1	9	58	60	3	5	9	43	-42

TABLE 38 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	5	9	46	42	-1	13	9	80	-83	0	3	10	129	128	1	9	10	109	-112	1	2	11	114	-110
3	6	9	31	-9	0	13	9	78	-78	1	3	10	148	151	3	9	10	79	72	2	2	11	31	27
-4	7	9	53	-54	1	13	9	29	29	3	3	10	83	-83	-4	10	10	36	-39	3	2	11	66	65
-3	7	9	86	-87	2	13	9	77	81	-3	4	10	39	36	-3	10	10	46	-51	-4	3	11	29	9
-1	7	9	136	138	-2	14	9	73	71	-1	4	10	101	-97	-1	10	10	59	59	-4	4	11	37	-27
0	7	9	136	144	-1	14	9	51	54	0	4	10	57	-56	-2	11	10	44	40	-2	4	11	127	128
1	7	9	49	-54	0	14	9	59	-58	1	4	10	42	51	-1	11	10	28	-6	-1	4	11	51	57
2	7	9	104	-101	1	14	9	75	-72	2	4	10	64	59	1	11	10	63	-71	0	4	11	76	-77
-4	8	9	71	81	-1	15	9	29	-6	-4	5	10	36	42	-3	12	10	77	-79	1	4	11	120	-118
-3	8	9	48	-55	-1	16	9	53	62	-2	5	10	93	-89	-1	12	10	72	65	3	4	11	62	59
-2	8	9	119	-119	0	16	9	58	-55	-1	5	10	49	-53	0	12	10	90	86	-4	5	11	68	-45
-1	8	9	49	-43	-4	0	10	97	-101	0	5	10	42	40	1	12	10	45	-29	-3	5	11	96	-96
0	8	9	83	84	-3	0	10	125	-127	1	5	10	85	85	2	12	10	88	-92	-1	5	11	127	124
1	8	9	112	111	-1	0	10	119	117	-4	6	10	52	49	-2	13	10	44	-48	0	5	11	63	64
2	8	9	37	36	0	0	10	96	94	-3	6	10	107	107	-1	13	10	40	-34	1	5	11	74	-70
3	8	9	74	-71	1	0	10	31	-41	-1	6	10	156	-151	0	13	10	43	43	2	5	11	83	-89
-2	9	9	44	-47	2	0	10	146	-148	0	6	10	95	-95	-1	14	10	32	34	0	6	11	26	-23
0	9	9	49	42	3	0	10	37	-37	1	6	10	89	88	0	14	10	45	43	-4	7	11	49	-41
-4	10	9	67	67	-4	1	10	52	48	2	6	10	111	115	-2	15	10	105	-101	-3	7	11	100	-103
-3	10	9	44	-41	-2	1	10	70	-76	3	6	10	30	35	-1	15	10	37	-39	-1	7	11	132	134
-2	10	9	104	-99	-1	1	10	43	-48	-2	7	10	60	66	0	15	10	73	74	0	7	11	53	46
-1	10	9	27	-22	0	1	10	66	70	0	7	10	39	-35	-4	1	11	91	92	1	7	11	66	-65
0	10	9	72	74	1	1	10	66	69	1	7	10	53	-59	-3	1	11	91	88	2	7	11	81	-82
1	10	9	107	110	3	1	10	44	-45	3	7	10	32	39	-2	1	11	31	-25	-4	8	11	38	36
2	10	9	30	25	-4	2	10	55	-58	-3	8	10	80	78	-1	1	11	115	-108	-3	8	11	51	-46
3	10	9	74	-71	-3	2	10	61	-64	-2	8	10	29	22	0	1	11	75	-75	-2	8	11	99	-92
-4	11	9	35	41	-1	2	10	56	59	-1	8	10	65	-64	1	1	11	40	28	-1	8	11	31	-33
-3	11	9	95	92	0	2	10	49	53	0	8	10	65	-69	2	1	11	126	122	0	8	11	57	49
-1	11	9	86	-80	2	2	10	62	-53	1	8	10	37	38	3	1	11	31	34	1	8	11	96	93
0	11	9	74	-70	-5	3	10	66	68	2	8	10	40	44	-4	2	11	59	-59	-3	9	11	30	-18
1	11	9	32	24	-4	3	10	72	67	3	8	10	30	21	-3	2	11	40	33	-2	10	11	63	-60
2	11	9	84	78	-3	3	10	36	-35	-4	9	10	67	-72	-2	2	11	113	111	-1	10	11	27	-17
3	11	9	35	24	-2	3	10	165	-159	-2	9	10	115	109	-1	2	11	47	51	0	10	11	54	58
-2	13	9	61	66	-1	3	10	62	-55	0	9	10	79	-79	0	2	11	111	-111	1	10	11	87	84

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	11	11	58	53	3	3	12	79	-77	1	12	12	43	-41	1	8	13	65	66	-1	6	14	93	-90
-2	11	11	32	-16	-3	4	12	71	66	0	13	12	58	49	-1	9	13	29	10	0	6	14	52	-49
-1	11	11	78	-81	-1	4	12	86	-84	-4	1	13	60	62	-2	10	13	58	-66	-3	7	14	52	40
0	11	11	54	-52	2	4	12	40	32	-3	1	13	52	51	-1	10	13	35	-31	-2	7	14	30	26
1	11	11	34	34	-3	5	12	33	-31	-1	1	13	90	-89	0	10	13	49	43	0	7	14	58	-58
2	11	11	90	81	-2	5	12	71	-72	0	1	13	76	-75	1	10	13	75	68	-2	8	14	35	-23
-1	13	11	72	-67	0	5	12	71	67	1	1	13	71	66	-1	11	13	74	-73	-1	8	14	59	-53
0	13	11	53	-50	1	5	12	42	42	2	1	13	107	99	-1	12	13	32	-27	0	8	14	32	-27
-2	14	11	81	92	-4	6	12	51	57	-3	2	13	51	48	-3	0	14	56	-43	-2	9	14	85	79
0	14	11	73	-75	-3	6	12	113	115	-2	2	13	100	102	-1	0	14	109	106	0	9	14	85	-74
-4	0	12	79	-77	-1	6	12	121	-121	0	2	13	95	-89	0	0	14	86	87	-2	1	15	31	-26
-3	0	12	79	-79	0	6	12	42	-47	1	2	13	45	-46	1	0	14	98	-91	-1	1	15	88	-82
-2	0	12	32	32	1	6	12	61	65	2	2	13	32	21	2	0	14	84	-80	0	1	15	35	-46
-1	0	12	130	122	2	6	12	85	79	0	3	13	31	-35	-3	1	14	33	-32	1	1	15	54	51
0	0	12	91	88	-3	7	12	43	39	-4	4	13	44	-44	-2	1	14	51	-49	-3	2	15	49	50
1	0	12	33	-44	-2	7	12	41	35	-3	4	13	58	61	0	1	14	49	55	-2	2	15	63	78
2	0	12	134	-134	1	7	12	53	-50	-2	4	13	105	98	1	1	14	39	39	0	2	15	50	-55
-2	1	12	63	-59	-3	8	12	42	43	0	4	13	98	-95	-1	2	14	36	35	1	2	15	65	-70
0	1	12	53	57	-1	8	12	92	-93	1	4	13	52	-49	0	2	14	36	42	-2	4	15	80	74
1	1	12	57	57	2	8	12	44	43	2	4	13	33	1	1	2	14	40	-38	0	4	15	71	-67
3	1	12	33	-38	-3	9	12	48	57	-3	5	13	82	-78	2	2	14	43	-41	1	4	15	51	-52
-4	2	12	54	-52	-2	9	12	85	84	-1	5	13	104	109	-3	3	14	62	-65	-2	5	15	42	49
-3	2	12	48	-49	-1	9	12	43	37	1	5	13	46	-43	-2	3	14	103	-98	-1	5	15	80	71
-1	2	12	40	38	0	9	12	75	-67	2	5	13	52	-49	0	3	14	97	92	1	5	15	39	-29
0	2	12	54	56	1	9	12	90	-85	-3	7	13	80	-75	1	3	14	73	63	-2	7	15	42	32
2	2	12	82	-82	-3	10	12	36	-32	-1	7	13	98	94	-3	4	14	34	35	-1	7	15	77	75
-4	3	12	45	44	-1	10	12	61	64	0	7	13	63	62	-2	4	14	33	-28	-2	0	16	34	27
-3	3	12	57	-51	1	10	12	40	-32	1	7	13	52	-46	-1	4	14	60	-55	-1	0	16	105	95
-2	3	12	134	-128	-2	11	12	34	31	2	7	13	54	-61	1	4	14	32	30	-2	1	16	49	-38
-1	3	12	36	-36	-1	11	12	48	47	-3	8	13	52	-56	-2	5	14	57	-58	0	1	16	41	35
0	3	12	101	94	1	11	12	43	-49	-2	8	13	72	-69	0	5	14	31	30	-1	2	16	41	50
1	3	12	89	85	-1	12	12	95	92	-1	8	13	38	-29	-3	6	14	74	68	-1	4	16	39	-39
2	3	12	32	-22	0	12	12	55	49	0	8	13	81	73	-2	6	14	32	-27					

TABLE 39 : OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (58)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	0	0	80	-96	8	1	0	87	88	13	2	0	16	16	-11	4	0	47	-50	-3	5	0	114	-112
4	0	0	103	-122	9	1	0	46	45	14	2	0	18	15	-10	4	0	44	-45	-2	5	0	73	-71
5	0	0	133	-150	10	1	0	7	5	15	2	0	18	10	-9	4	0	25	-25	-1	5	0	13	-11
6	0	0	60	-70	11	1	0	25	-22	-15	3	0	16	13	-8	4	0	24	25	0	5	0	47	47
7	0	0	17	16	12	1	0	52	-48	-14	3	0	27	25	-7	4	0	50	53	1	5	0	123	118
8	0	0	71	72	13	1	0	46	-43	-13	3	0	30	29	-6	4	0	88	89	2	5	0	93	91
9	0	0	80	80	-16	2	0	24	-22	-12	3	0	19	21	-5	4	0	65	63	3	5	0	41	39
10	0	0	66	64	-15	2	0	16	-15	-10	3	0	33	-34	-4	4	0	9	10	4	5	0	42	-38
11	0	0	12	11	-13	2	0	24	24	-9	3	0	69	-72	-3	4	0	57	-55	5	5	0	64	-61
12	0	0	22	-20	-12	2	0	38	41	-8	3	0	47	-49	-2	4	0	112	-106	6	5	0	55	-50
13	0	0	50	-44	-11	2	0	39	43	-6	3	0	25	28	-1	4	0	77	-73	7	5	0	56	-52
14	0	0	30	-24	-10	2	0	14	16	-5	3	0	75	77	0	4	0	59	-52	8	5	0	15	-14
15	0	0	23	-19	-9	2	0	21	-20	-4	3	0	75	80	1	4	0	22	24	9	5	0	28	27
-16	1	0	21	-19	-8	2	0	55	-56	-3	3	0	69	70	2	4	0	81	82	10	5	0	50	48
-15	1	0	27	-24	-7	2	0	64	-66	-2	3	0	25	-22	3	4	0	87	87	11	5	0	33	31
-14	1	0	32	-30	-6	2	0	106	-110	-1	3	0	90	-83	4	4	0	68	66	12	5	0	10	9
-13	1	0	10	-12	-5	2	0	6	-2	0	3	0	102	-97	6	4	0	34	-31	-15	6	0	20	-21
-12	1	0	24	25	-4	2	0	105	109	1	3	0	75	-70	7	4	0	86	-81	-14	6	0	29	-29
-11	1	0	49	53	-3	2	0	123	126	2	3	0	13	-10	8	4	0	63	-60	-13	6	0	37	-40
-10	1	0	61	66	-2	2	0	67	67	3	3	0	55	56	9	4	0	12	-8	-12	6	0	20	-23
-9	1	0	42	46	-1	2	0	85	80	4	3	0	79	79	10	4	0	18	21	-11	6	0	17	17
-8	1	0	16	-15	0	2	0	76	-70	5	3	0	58	58	11	4	0	32	30	-10	6	0	54	55
-7	1	0	69	-79	1	2	0	131	-124	6	3	0	36	37	12	4	0	28	25	-9	6	0	69	70
-6	1	0	108	-125	2	2	0	141	-136	8	3	0	61	-59	13	4	0	20	16	-8	6	0	62	61
-5	1	0	87	-99	3	2	0	65	-64	9	3	0	40	-37	-14	5	0	13	-13	-7	6	0	7	3
-4	1	0	6	7	4	2	0	7	-5	10	3	0	27	-22	-13	5	0	26	-28	-6	6	0	47	-50
-3	1	0	100	105	5	2	0	78	78	11	3	0	17	-18	-12	5	0	44	-46	-5	6	0	92	-95
-2	1	0	81	81	6	2	0	91	92	13	3	0	35	32	-11	5	0	30	-32	-4	6	0	100	-102
2	1	0	68	-71	7	2	0	78	78	14	3	0	30	27	-9	5	0	42	43	-3	6	0	65	-66
3	1	0	172	-184	8	2	0	14	14	15	3	0	15	9	-8	5	0	75	75	-2	6	0	34	30
4	1	0	104	-114	9	2	0	18	-19	-15	4	0	24	22	-7	5	0	79	78	-1	6	0	93	90
5	1	0	38	-43	10	2	0	46	-47	-14	4	0	21	22	-6	5	0	43	41	0	6	0	126	121
6	1	0	34	35	11	2	0	51	-50	-13	4	0	9	9	-5	5	0	32	-32	1	6	0	77	75
7	1	0	86	89	12	2	0	32	-29	-12	4	0	28	-31	-4	5	0	93	-91	2	6	0	19	16

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	6	0	40	-41	-13	8	0	21	20	3	9	0	18	20	-5	12	0	30	-36	10	-10	1	22	21
4	6	0	86	-85	-12	8	0	33	33	4	9	0	33	34	-4	12	0	34	-38	-9	-9	1	27	25
5	6	0	79	-78	-11	8	0	30	31	5	9	0	38	40	-3	12	0	18	-21	-8	-9	1	39	39
6	6	0	35	-34	-10	8	0	13	13	6	9	0	17	17	-1	12	0	29	32	-7	-9	1	23	22
7	6	0	10	9	-8	8	0	53	-54	8	9	0	23	-23	0	12	0	33	38	-5	-9	1	14	-14
8	6	0	41	39	-7	8	0	57	-58	9	9	0	21	-22	1	12	0	25	28	-4	-9	1	42	-43
9	6	0	48	45	-6	8	0	50	-51	-11	10	0	21	-21	1	-12	1	43	-44	-3	-9	1	42	-45
10	6	0	35	34	-4	8	0	63	64	-10	10	0	30	-31	2	-12	1	20	-20	-2	-9	1	32	-32
12	6	0	12	-11	-3	8	0	74	76	-9	10	0	25	-26	-4	-11	1	18	20	0	-9	1	46	45
13	6	0	27	-23	-2	8	0	51	53	-8	10	0	10	12	-3	-11	1	11	-10	1	-9	1	63	64
-14	7	0	22	-20	-1	8	0	17	19	-7	10	0	32	35	-2	-11	1	33	-33	2	-9	1	46	46
-12	7	0	18	18	0	8	0	28	-29	-6	10	0	35	39	-1	-11	1	37	-39	3	-9	1	12	11
-11	7	0	46	45	1	8	0	58	-60	-5	10	0	28	31	0	-11	1	33	-37	4	-9	1	34	-33
-10	7	0	51	53	2	8	0	62	-63	-3	10	0	22	-23	1	-11	1	21	-20	5	-9	1	54	-54
-9	7	0	31	32	3	8	0	36	-37	-2	10	0	44	-46	2	-11	1	19	20	6	-9	1	51	-51
-8	7	0	11	-12	5	8	0	38	37	-1	10	0	41	-43	3	-11	1	41	45	7	-9	1	27	-27
-7	7	0	55	-57	6	8	0	41	40	0	10	0	17	-17	4	-11	1	50	52	9	-9	1	45	42
-6	7	0	71	-73	7	8	0	39	37	2	10	0	29	31	5	-11	1	29	30	10	-9	1	40	37
-5	7	0	75	-78	8	8	0	16	17	3	10	0	41	43	7	-11	1	31	-30	11	-9	1	24	24
-3	7	0	40	40	9	8	0	15	-14	4	10	0	28	30	-7	-10	1	27	29	-10	-8	1	20	21
-2	7	0	67	68	10	8	0	20	-21	6	10	0	19	-18	-6	-10	1	28	30	-9	-8	1	32	31
-1	7	0	86	85	-12	9	0	15	17	7	10	0	23	-22	-5	-10	1	29	30	-8	-8	1	25	23
0	7	0	83	80	-10	9	0	31	-31	-9	11	0	17	18	-4	-10	1	15	-14	-7	-8	1	16	-14
1	7	0	8	-6	-9	9	0	39	-41	-8	11	0	36	40	-3	-10	1	55	-56	-6	-8	1	25	-26
2	7	0	56	-58	-8	9	0	21	-20	-7	11	0	29	31	-2	-10	1	56	-57	-5	-8	1	52	-53
3	7	0	80	-81	-6	9	0	9	-4	-6	11	0	16	14	-1	-10	1	26	-29	-4	-8	1	50	-50
4	7	0	66	-67	-5	9	0	39	43	-5	11	0	10	-10	1	-10	1	38	39	-2	-8	1	36	35
5	7	0	24	-25	-4	9	0	52	57	-4	11	0	30	-34	2	-10	1	60	62	-1	-8	1	59	57
6	7	0	29	26	-3	9	0	28	31	-3	11	0	39	-44	3	-10	1	49	51	0	-8	1	58	57
7	7	0	44	43	-2	9	0	11	-11	-2	11	0	26	-29	4	-10	1	20	21	1	-8	1	34	33
8	7	0	50	47	-1	9	0	33	-33	0	11	0	23	26	5	-10	1	18	-17	2	-8	1	12	-14
9	7	0	27	25	0	9	0	51	-52	1	11	0	32	35	6	-10	1	46	-46	3	-8	1	54	-53
11	7	0	16	-17	1	9	0	41	-42	2	11	0	29	33	7	-10	1	53	-52	4	-8	1	58	-58
12	7	0	25	-22	2	9	0	11	-12	5	11	0	19	-19	8	-10	1	35	-34	5	-8	1	43	-43

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	-8	1	26	23	-4	-6	1	77	76	3	-5	1	82	81	8	-4	1	70	-64	12	-3	1	13	11
8	-8	1	56	52	-3	-6	1	65	63	4	-5	1	110	103	9	-4	1	11	-9	13	-3	1	22	-18
9	-8	1	47	45	-2	-6	1	25	22	5	-5	1	78	72	10	-4	1	40	38	14	-3	1	29	-22
11	-8	1	9	-10	-1	-6	1	35	-34	6	-5	1	7	-7	11	-4	1	61	58	15	-3	1	30	-26
12	-8	1	22	-20	0	-6	1	87	-84	7	-5	1	54	-51	12	-4	1	50	48	-15	-2	1	19	-18
-11	-7	1	22	22	1	-6	1	93	-88	8	-5	1	81	-75	13	-4	1	18	15	-14	-2	1	27	-24
-10	-7	1	13	14	2	-6	1	63	-58	9	-5	1	62	-59	14	-4	1	10	-10	-13	-2	1	24	-25
-8	-7	1	25	-24	3	-6	1	11	-9	10	-5	1	23	-22	15	-4	1	22	-18	-11	-2	1	18	16
-7	-7	1	47	-47	4	-6	1	70	66	11	-5	1	21	20	-14	-3	1	16	-14	-10	-2	1	43	43
-6	-7	1	31	-33	5	-6	1	105	98	12	-5	1	43	38	-13	-3	1	32	-31	-9	-2	1	65	69
-5	-7	1	23	-22	6	-6	1	67	62	13	-5	1	39	34	-12	-3	1	34	-35	-8	-2	1	53	54
-4	-7	1	29	26	7	-6	1	13	7	14	-5	1	23	19	-11	-3	1	23	-26	-7	-2	1	23	-26
-3	-7	1	47	46	8	-6	1	33	-32	-14	-4	1	13	9	-10	-3	1	12	9	-6	-2	1	84	-87
-2	-7	1	69	66	9	-6	1	58	-54	-13	-4	1	15	-14	-9	-3	1	60	60	-5	-2	1	78	-80
-1	-7	1	45	43	10	-6	1	36	-35	-12	-4	1	35	-35	-8	-3	1	71	71	-4	-2	1	81	-79
1	-7	1	44	-44	11	-6	1	27	-25	-11	-4	1	44	-43	-7	-3	1	49	47	-2	-2	1	57	51
2	-7	1	56	-58	13	-6	1	27	23	-10	-4	1	33	-33	-6	-3	1	8	-6	-1	-2	1	123	107
3	-7	1	69	-69	14	-6	1	30	26	-9	-4	1	8	6	-5	-3	1	17	-17	0	-2	1	107	95
4	-7	1	18	-19	-13	-5	1	14	14	-8	-4	1	41	42	-4	-3	1	104	-101	1	-2	1	58	51
5	-7	1	39	34	-12	-5	1	10	-10	-7	-4	1	82	82	-3	-3	1	135	-125	2	-2	1	12	-13
6	-7	1	48	44	-11	-5	1	28	-28	-6	-4	1	81	81	-2	-3	1	65	-60	3	-2	1	92	-85
7	-7	1	25	21	-10	-5	1	47	-47	-5	-4	1	35	35	-1	-3	1	33	29	4	-2	1	107	-101
8	-7	1	52	49	-9	-5	1	41	-39	-4	-4	1	42	-39	0	-3	1	137	121	5	-2	1	77	-74
9	-7	1	17	12	-8	-5	1	13	-11	-3	-4	1	125	-113	1	-3	1	128	116	6	-2	1	8	-10
10	-7	1	28	-26	-7	-5	1	31	33	-2	-4	1	132	-119	2	-3	1	110	99	7	-2	1	45	46
11	-7	1	44	-41	-6	-5	1	73	74	-1	-4	1	110	-95	3	-3	1	20	20	8	-2	1	54	54
12	-7	1	28	-26	-5	-5	1	89	88	0	-4	1	16	-11	4	-3	1	74	-66	9	-2	1	65	64
-12	-6	1	18	14	-4	-5	1	49	49	1	-4	1	103	95	5	-3	1	116	-107	10	-2	1	22	25
-10	-6	1	16	-14	-3	-5	1	19	-16	2	-4	1	155	142	6	-3	1	112	-104	12	-2	1	36	-34
-9	-6	1	42	-40	-2	-5	1	93	-83	3	-4	1	143	130	7	-3	1	41	-38	13	-2	1	41	-38
-8	-6	1	52	-49	-1	-5	1	132	-120	4	-4	1	31	33	8	-3	1	11	12	14	-2	1	22	-16
-7	-6	1	24	-23	0	-5	1	112	-98	5	-4	1	35	-31	9	-3	1	55	54	-15	-1	1	27	-24
-6	-6	1	9	10	1	-5	1	14	10	6	-4	1	92	-85	10	-3	1	64	63	-13	-1	1	14	16
-5	-6	1	47	46	2	-5	1	33	35	7	-4	1	105	-97	11	-3	1	43	41	-12	-1	1	46	46

TABLE 39 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-11	-1	1	22	19	-7	0	1	51	-57	-4	1	1	65	68	-1	2	1	207	-181	5	3	1	92	-87
-10	-1	1	23	20	-6	0	1	11	12	-3	1	1	14	-11	0	2	1	31	-26	6	3	1	85	-80
-9	-1	1	18	20	-5	0	1	69	78	-2	1	1	146	-134	1	2	1	257	237	7	3	1	47	-45
-8	-1	1	23	-25	-4	0	1	104	117	-1	1	1	116	-105	2	2	1	126	119	8	3	1	11	12
-7	-1	1	76	-85	-3	0	1	81	91	0	1	1	136	-126	3	2	1	94	92	9	3	1	43	43
-6	-1	1	50	-56	-2	0	1	43	46	1	1	1	9	-3	4	2	1	35	36	10	3	1	45	43
-5	-1	1	38	-41	-1	0	1	43	-50	2	1	1	12	11	5	2	1	20	-17	11	3	1	37	37
-4	-1	1	9	5	0	0	1	110	-121	3	1	1	59	59	6	2	1	89	-87	12	3	1	13	16
-3	-1	1	71	69	1	0	1	120	-143	4	1	1	131	136	7	2	1	85	-86	13	3	1	17	-15
-2	-1	1	119	110	2	0	1	12	-11	5	1	1	79	84	8	2	1	52	-52	14	3	1	28	-24
-1	-1	1	73	64	3	0	1	38	-42	6	1	1	7	3	10	2	1	29	29	-15	4	1	23	-20
0	-1	1	50	40	4	0	1	81	83	7	1	1	55	-59	11	2	1	51	48	-14	4	1	30	-29
1	-1	1	70	-68	5	0	1	113	118	8	1	1	73	-76	12	2	1	36	33	-13	4	1	28	-27
2	-1	1	95	-94	6	0	1	61	61	9	1	1	56	-55	13	2	1	12	13	-12	4	1	11	-11
3	-1	1	83	-85	7	0	1	10	-11	10	1	1	17	-17	-16	3	1	19	16	-11	4	1	27	24
4	-1	1	22	-25	8	0	1	16	-19	11	1	1	18	18	-14	3	1	20	-18	-10	4	1	52	50
5	-1	1	23	23	9	0	1	44	-44	12	1	1	37	33	-13	3	1	43	-41	-9	4	1	57	54
6	-1	1	61	62	10	0	1	45	-44	13	1	1	41	35	-12	3	1	45	-46	-8	4	1	39	37
7	-1	1	59	60	11	0	1	27	-25	14	1	1	18	13	-11	3	1	22	-23	-6	4	1	47	-45
8	-1	1	55	54	13	0	1	23	19	-16	2	1	31	26	-10	3	1	19	19	-5	4	1	138	-132
10	-1	1	37	-37	14	0	1	33	26	-15	2	1	25	22	-9	3	1	61	61	-4	4	1	79	-75
11	-1	1	38	-37	15	0	1	20	14	-14	2	1	8	7	-8	3	1	91	90	-2	4	1	63	58
12	-1	1	33	-29	-16	1	1	17	17	-13	2	1	12	-10	-7	3	1	58	58	-1	4	1	91	82
13	-1	1	14	-12	-15	1	1	29	27	-12	2	1	50	-49	-6	3	1	7	10	0	4	1	114	107
14	-1	1	8	7	-14	1	1	26	23	-11	2	1	57	-58	-5	3	1	86	-81	1	4	1	57	55
15	-1	1	22	17	-13	1	1	26	27	-10	2	1	44	-46	-4	3	1	128	-117	2	4	1	27	-25
-16	0	1	11	-5	-12	1	1	21	-23	-9	2	1	9	9	-3	3	1	86	-77	3	4	1	78	-74
-15	0	1	9	4	-11	1	1	45	-46	-8	2	1	52	58	-2	3	1	40	-35	4	4	1	88	-81
-14	0	1	8	5	-10	1	1	56	-57	-7	2	1	99	106	-1	3	1	8	-2	5	4	1	69	-66
-13	0	1	33	33	-9	1	1	54	-55	-6	2	1	100	103	0	3	1	87	81	6	4	1	11	-9
-12	0	1	49	52	-8	1	1	20	-19	-5	2	1	43	43	1	3	1	141	129	7	4	1	29	30
-10	0	1	25	-28	-7	1	1	43	48	-4	2	1	76	-69	2	3	1	113	109	8	4	1	56	57
-9	0	1	59	-63	-6	1	1	91	102	-3	2	1	109	-97	3	3	1	26	28	9	4	1	38	37
-8	0	1	62	-68	-5	1	1	103	113	-2	2	1	186	-162	4	3	1	69	-63	10	4	1	23	24

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
12	4	1	27	-26	-5	6	1	45	43	5	7	1	25	22	-3	9	1	45	-44	4	11	1	11	-11
13	4	1	27	-24	-4	6	1	75	68	7	7	1	17	-15	-2	9	1	28	-28	-4	12	1	22	25
-15	5	1	24	-22	-3	6	1	67	64	8	7	1	37	-36	0	9	1	42	43	-3	12	1	25	25
-12	5	1	29	26	-2	6	1	27	23	9	7	1	33	-32	1	9	1	63	64	-2	12	1	12	11
-11	5	1	42	40	-1	6	1	28	-29	11	7	1	13	12	2	9	1	38	40	-1	11	2	27	27
-10	5	1	37	34	0	6	1	51	-50	-13	8	1	11	-10	3	9	1	8	9	0	11	2	32	35
-9	5	1	12	11	1	6	1	78	-77	-12	8	1	36	-36	4	9	1	23	-23	1	11	2	26	28
-8	5	1	42	-41	2	6	1	37	-39	-11	8	1	43	-42	5	9	1	42	-41	3	11	2	18	-17
-7	5	1	54	-54	4	6	1	37	35	-10	8	1	28	-24	6	9	1	36	-35	4	11	2	27	-29
-6	5	1	55	-55	5	6	1	57	54	-8	8	1	38	37	7	9	1	14	-13	-5	10	2	21	-23
-5	5	1	37	-36	6	6	1	47	44	-7	8	1	66	67	-10	10	1	28	27	-3	10	2	26	27
-4	5	1	14	11	7	6	1	22	19	-6	8	1	48	47	-9	10	1	33	32	-2	10	2	36	36
-3	5	1	63	59	8	6	1	21	-24	-5	8	1	27	29	-8	10	1	26	27	-1	10	2	39	40
-2	5	1	98	91	9	6	1	35	-34	-4	8	1	27	-25	-7	10	1	13	-11	0	10	2	25	24
-1	5	1	53	48	10	6	1	25	-22	-3	8	1	65	-64	-6	10	1	31	-32	1	10	2	11	-11
0	5	1	10	6	11	6	1	10	-9	-2	8	1	78	-77	-5	10	1	53	-56	2	10	2	51	-49
1	5	1	43	-42	-14	7	1	20	17	-1	8	1	46	-44	-4	10	1	34	-34	3	10	2	44	-44
2	5	1	75	-74	-13	7	1	15	15	1	8	1	46	47	-2	10	1	25	27	4	10	2	26	-27
3	5	1	55	-55	-11	7	1	33	-31	2	8	1	55	55	-1	10	1	37	40	5	10	2	9	-5
4	5	1	24	-23	-10	7	1	47	-44	3	8	1	50	51	0	10	1	38	40	6	10	2	22	21
5	5	1	16	15	-9	7	1	43	-41	4	8	1	24	23	1	10	1	18	19	7	10	2	34	36
6	5	1	36	33	-8	7	1	19	-17	5	8	1	15	-15	3	10	1	29	-28	-7	9	2	30	-33
7	5	1	52	49	-7	7	1	28	27	6	8	1	39	-39	4	10	1	34	-33	-6	9	2	15	-15
8	5	1	33	32	-6	7	1	61	61	7	8	1	34	-32	5	10	1	26	-25	-5	9	2	15	13
11	5	1	19	-17	-5	7	1	71	69	8	8	1	25	-24	-8	11	1	18	-19	-4	9	2	41	42
12	5	1	28	-25	-4	7	1	46	45	10	8	1	17	13	-7	11	1	16	-18	-3	9	2	56	54
13	5	1	17	-18	-3	7	1	9	-8	-12	9	1	28	-27	-6	11	1	18	-19	-2	9	2	28	30
-14	6	1	14	15	-2	7	1	49	-49	-11	9	1	15	-15	-5	11	1	24	-28	0	9	2	22	-25
-13	6	1	30	31	-1	7	1	67	-65	-10	9	1	14	12	-3	11	1	29	30	1	9	2	53	-55
-12	6	1	36	37	0	7	1	66	-64	-9	9	1	37	37	-2	11	1	31	34	2	9	2	61	-63
-10	6	1	19	-19	1	7	1	28	-29	-8	9	1	48	48	-1	11	1	22	22	3	9	2	29	-29
-9	6	1	44	-42	2	7	1	32	32	-7	9	1	29	31	1	11	1	16	-17	4	9	2	11	11
-8	6	1	54	-53	3	7	1	55	53	-5	9	1	29	-27	2	11	1	26	-27	5	9	2	49	48
-7	6	1	36	-35	4	7	1	56	54	-4	9	1	62	-65	3	11	1	22	-25	6	9	2	56	55

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
7	-9	2	40	38	3	-7	2	74	70	-11	-5	2	11	10	-2	-4	2	91	82	6	-3	2	90	86
8	-9	2	8	7	4	-7	2	64	63	-10	-5	2	23	21	-1	-4	2	91	81	7	-3	2	56	55
9	-9	2	20	-22	5	-7	2	22	21	-9	-5	2	38	35	0	-4	2	54	47	8	-3	2	13	12
-9	-8	2	37	-36	6	-7	2	20	-18	-8	-5	2	34	33	1	-4	2	20	-20	9	-3	2	26	-25
-8	-8	2	27	-27	7	-7	2	46	-45	-7	-5	2	8	13	2	-4	2	65	-60	10	-3	2	49	-47
-7	-8	2	12	-10	8	-7	2	56	-54	-6	-5	2	28	-26	3	-4	2	99	-90	11	-3	2	42	-41
-6	-8	2	17	17	9	-7	2	42	-40	-5	-5	2	54	-48	4	-4	2	83	-75	12	-3	2	20	-17
-5	-8	2	41	43	10	-7	2	9	8	-4	-5	2	69	-61	6	-4	2	49	49	14	-3	2	18	16
-4	-8	2	84	80	11	-7	2	21	18	-3	-5	2	36	-32	7	-4	2	63	61	-14	-2	2	30	28
-3	-8	2	37	35	12	-7	2	31	29	-2	-5	2	8	-2	8	-4	2	46	43	-13	-2	2	34	32
-2	-8	2	27	-25	-12	-6	2	24	-21	-1	-5	2	57	54	9	-4	2	16	15	-12	-2	2	20	18
-1	-8	2	56	-55	-11	-6	2	23	-21	0	-5	2	72	69	10	-4	2	13	-10	-11	-2	2	9	-11
0	-8	2	66	-65	-10	-6	2	21	-20	1	-5	2	55	54	11	-4	2	24	-21	-10	-2	2	41	-42
1	-8	2	57	-58	-8	-6	2	39	40	2	-5	2	19	19	12	-4	2	35	-31	-9	-2	2	61	-61
2	-8	2	14	-14	-7	-6	2	57	54	3	-5	2	16	-15	13	-4	2	22	-19	-8	-2	2	49	-50
3	-8	2	37	34	-6	-6	2	30	30	4	-5	2	79	-71	-14	-3	2	10	7	-7	-2	2	22	-21
4	-8	2	65	62	-5	-6	2	17	14	5	-5	2	57	-52	-13	-3	2	28	25	-6	-2	2	54	51
5	-8	2	63	61	-4	-6	2	52	-45	6	-5	2	16	-16	-12	-3	2	37	35	-5	-2	2	94	91
6	-8	2	38	36	-3	-6	2	81	-73	8	-5	2	7	6	-11	-3	2	24	23	-4	-2	2	103	102
8	-8	2	36	-36	-2	-6	2	61	-56	9	-5	2	55	53	-10	-3	2	9	2	-3	-2	2	67	59
9	-8	2	51	-49	-1	-6	2	26	-23	10	-5	2	39	39	-9	-3	2	35	-37	-2	-2	2	32	-29
10	-8	2	33	-32	0	-6	2	20	20	11	-5	2	9	10	-8	-3	2	58	-59	-1	-2	2	86	-82
11	-8	2	12	-11	1	-6	2	62	61	12	-5	2	19	-18	-7	-3	2	62	-63	0	-2	2	141	-130
-10	-7	2	36	-33	2	-6	2	74	70	13	-5	2	23	-22	-6	-3	2	33	-33	1	-2	2	112	-104
-9	-7	2	27	-27	3	-6	2	46	47	-12	-4	2	20	18	-5	-3	2	35	30	2	-2	2	25	-24
-7	-7	2	42	40	5	-6	2	40	-37	-11	-4	2	28	26	-4	-3	2	84	76	3	-2	2	69	61
-6	-7	2	43	42	6	-6	2	60	-56	-10	-4	2	37	35	-3	-3	2	116	102	4	-2	2	110	103
-5	-7	2	31	33	7	-6	2	47	-45	-9	-4	2	21	20	-2	-3	2	80	71	5	-2	2	84	82
-4	-7	2	34	32	8	-6	2	24	-23	-8	-4	2	19	-18	-1	-3	2	11	6	6	-2	2	57	55
-3	-7	2	19	-18	9	-6	2	27	24	-7	-4	2	51	-49	0	-3	2	79	-73	8	-2	2	48	-49
-2	-7	2	50	-51	10	-6	2	39	37	-6	-4	2	64	-61	1	-3	2	114	-104	9	-2	2	61	-62
-1	-7	2	82	-77	11	-6	2	23	21	-5	-4	2	50	-46	2	-3	2	63	-60	10	-2	2	48	-48
0	-7	2	50	-48	12	-6	2	19	16	-4	-4	2	10	-11	3	-3	2	64	-58	11	-2	2	13	-12
2	-7	2	49	46	-12	-5	2	12	-12	-3	-4	2	45	42	5	-3	2	67	63	12	-2	2	16	16

TABLE 39 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
13	-2	2	32	31	-10	0	2	24	-27	-2	1	2	11	-10	6	2	2	38	40	-13	4	2	32	29
14	-2	2	27	23	-8	0	2	63	68	-1	1	2	58	57	7	2	2	40	42	-12	4	2	24	23
-15	-1	2	26	23	-7	0	2	79	88	0	1	2	70	70	8	2	2	26	27	-11	4	2	11	-10
-14	-1	2	29	25	-6	0	2	37	43	1	1	2	87	93	9	2	2	20	21	-10	4	2	44	-44
-12	-1	2	13	-12	-5	0	2	11	-11	2	1	2	7	8	11	2	2	22	-19	-9	4	2	63	-61
-11	-1	2	44	-42	-4	0	2	43	-49	3	1	2	17	-15	12	2	2	27	-22	-8	4	2	50	-48
-10	-1	2	53	-54	-3	0	2	78	-90	4	1	2	62	-64	13	2	2	18	-14	-7	4	2	14	-14
-9	-1	2	42	-44	-2	0	2	66	-76	5	1	2	56	-59	-14	3	2	10	10	-6	4	2	44	40
-8	-1	2	10	12	-1	0	2	34	-34	6	1	2	32	-33	-13	3	2	25	24	-5	4	2	95	85
-7	-1	2	49	54	0	0	2	24	26	8	1	2	26	26	-12	3	2	46	44	-4	4	2	97	87
-6	-1	2	66	69	1	0	2	64	74	9	1	2	45	47	-11	3	2	22	18	-3	4	2	44	36
-5	-1	2	57	61	2	0	2	75	87	10	1	2	29	28	-9	3	2	30	-31	-2	4	2	17	12
-4	-1	2	70	69	3	0	2	50	55	12	1	2	9	-8	-8	3	2	61	-59	-1	4	2	81	-76
-3	-1	2	37	-38	4	0	2	11	11	13	1	2	21	-17	-7	3	2	68	-66	0	4	2	145	-137
-2	-1	2	109	-103	5	0	2	50	-52	-15	2	2	19	-13	-6	3	2	29	-28	1	4	2	82	-79
-1	-1	2	120	-113	6	0	2	62	-68	-14	2	2	20	-16	-5	3	2	19	18	2	4	2	32	30
0	-1	2	71	-69	7	0	2	46	-49	-13	2	2	16	-20	-4	3	2	81	74	3	4	2	37	33
1	-1	2	10	6	8	0	2	21	-18	-12	2	2	22	20	-3	3	2	97	88	4	4	2	58	55
2	-1	2	72	69	10	0	2	39	37	-11	2	2	52	54	-2	3	2	74	68	5	4	2	63	58
3	-1	2	102	101	11	0	2	36	34	-10	2	2	37	38	0	3	2	38	-34	6	4	2	40	40
4	-1	2	86	86	12	0	2	25	24	-9	2	2	24	24	1	3	2	85	-80	8	4	2	32	-31
5	-1	2	32	31	14	0	2	17	-16	-8	2	2	16	-16	2	3	2	57	-51	9	4	2	41	-39
6	-1	2	27	-28	-14	1	2	30	-28	-7	2	2	47	-47	3	3	2	64	-62	10	4	2	28	-26
7	-1	2	63	-69	-13	1	2	31	-29	-6	2	2	79	-79	4	3	2	11	-10	11	4	2	10	-10
8	-1	2	55	-57	-12	1	2	16	-13	-5	2	2	61	-58	5	3	2	57	56	12	4	2	11	11
9	-1	2	41	-42	-11	1	2	21	23	-4	2	2	10	-8	6	3	2	67	67	-14	5	2	24	23
11	-1	2	26	25	-10	1	2	10	3	-3	2	2	45	43	7	3	2	44	44	-13	5	2	10	9
12	-1	2	37	33	-9	1	2	37	39	-2	2	2	83	77	8	3	2	9	9	-12	5	2	16	-14
13	-1	2	31	26	-8	1	2	54	61	-1	2	2	96	90	9	3	2	22	-22	-11	5	2	43	-41
14	-1	2	11	10	-7	1	2	25	29	0	2	2	50	51	10	3	2	33	-31	-10	5	2	50	-46
-15	0	2	18	16	-6	1	2	31	-31	1	2	2	33	-28	11	3	2	30	-27	-9	5	2	32	-30
-13	0	2	14	-13	-5	1	2	51	-53	2	2	2	71	-68	12	3	2	14	-12	-7	5	2	56	51
-12	0	2	41	-39	-4	1	2	77	-78	3	2	2	52	-46	-15	4	2	14	15	-6	5	2	72	64
-11	0	2	40	-40	-3	1	2	62	-62	4	2	2	83	-82	-14	4	2	30	26	-5	5	2	72	64

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-4	5	2	10	6	7	6	2	33	-31	0	8	2	21	22	-5	11	2	26	27	2	-7	3	17	-17
-3	5	2	35	-33	8	6	2	10	-11	2	8	2	31	-30	-3	11	2	11	-16	3	-7	3	53	-53
-2	5	2	55	-52	9	6	2	11	12	3	8	2	33	-30	-2	11	2	21	-21	4	-7	3	58	-55
-1	5	2	71	-68	10	6	2	16	16	4	8	2	27	-27	-1	11	2	28	-31	5	-7	3	37	-35
0	5	2	64	-59	-13	7	2	24	-18	6	8	2	14	12	0	11	2	21	-24	7	-7	3	29	29
1	5	2	13	-13	-12	7	2	21	-19	7	8	2	24	23	-3	-9	3	27	-27	8	-7	3	41	40
2	5	2	56	49	-10	7	2	21	19	8	8	2	21	22	-2	-9	3	34	-34	9	-7	3	33	33
3	5	2	79	75	-9	7	2	38	36	-11	9	2	21	20	-1	-9	3	28	-27	-10	-6	3	23	21
4	5	2	58	55	-8	7	2	35	36	-9	9	2	16	-15	1	-9	3	20	21	-8	-6	3	30	-27
5	5	2	22	19	-6	7	2	15	-12	-8	9	2	31	-31	2	-9	3	36	36	-7	-6	3	41	-38
6	5	2	13	-15	-5	7	2	38	-33	-7	9	2	37	-37	3	-9	3	33	31	-6	-6	3	48	-44
7	5	2	38	-37	-4	7	2	53	-49	-6	9	2	18	-16	4	-9	3	16	16	-5	-6	3	33	-30
8	5	2	42	-43	-3	7	2	38	-36	-4	9	2	31	32	-5	-8	3	30	-27	-3	-6	3	80	78
9	5	2	20	-21	-1	7	2	35	36	-3	9	2	40	42	-4	-8	3	39	-38	-2	-6	3	66	63
11	5	2	11	9	0	7	2	44	41	-2	9	2	28	27	-3	-8	3	35	-33	-1	-6	3	32	33
-13	6	2	17	-15	1	7	2	42	41	-1	9	2	11	11	-2	-8	3	9	-6	1	-6	3	40	-36
-12	6	2	35	-36	2	7	2	13	13	0	9	2	16	-14	-1	-8	3	11	11	2	-6	3	69	-64
-11	6	2	38	-35	3	7	2	17	-17	1	9	2	36	-36	0	-8	3	40	40	3	-6	3	57	-55
-10	6	2	15	-12	4	7	2	31	-28	2	9	2	34	-35	1	-8	3	56	52	4	-6	3	26	-24
-9	6	2	12	10	5	7	2	33	-31	3	9	2	12	-14	2	-8	3	32	29	5	-6	3	15	15
-8	6	2	39	36	6	7	2	21	-18	5	9	2	17	19	3	-8	3	14	-12	6	-6	3	42	42
-7	6	2	55	50	8	7	2	18	17	6	9	2	17	18	4	-8	3	25	-26	7	-6	3	51	51
-6	6	2	53	50	9	7	2	22	20	-9	10	2	29	-29	5	-8	3	34	-36	8	-6	3	31	30
-5	6	2	12	12	-12	8	2	12	13	-8	10	2	24	-24	6	-8	3	31	-32	10	-6	3	22	-22
-4	6	2	63	-59	-11	8	2	31	30	-6	10	2	21	21	7	-8	3	12	-14	-11	-5	3	13	15
-3	6	2	70	-64	-10	8	2	27	23	-5	10	2	31	29	-8	-7	3	11	8	-9	-5	3	31	-30
-2	6	2	51	-47	-9	8	2	17	16	-4	10	2	41	42	-7	-7	3	17	-15	-8	-5	3	49	-47
-1	6	2	20	-18	-7	8	2	29	-24	-3	10	2	20	18	-6	-7	3	42	-39	-7	-5	3	33	-31
0	6	2	17	13	-6	8	2	40	-38	-1	10	2	27	-29	-5	-7	3	41	-41	-5	-5	3	15	16
1	6	2	56	54	-5	8	2	34	-31	0	10	2	35	-35	-4	-7	3	32	-30	-4	-5	3	41	40
2	6	2	65	63	-4	8	2	15	-15	1	10	2	23	-26	-2	-7	3	43	41	-3	-5	3	69	65
3	6	2	33	30	-3	8	2	20	20	3	10	2	11	9	-1	-7	3	43	43	-2	-5	3	42	39
5	6	2	29	-28	-2	8	2	38	38	4	10	2	22	24	0	-7	3	49	49	0	-5	3	59	-55
6	6	2	42	-43	-1	8	2	39	39	-6	11	2	26	25	1	-7	3	27	25	1	-5	3	69	-66

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	-5	3	55	-53	-4	-3	3	48	46	5	-2	3	60	-61	-7	0	3	51	-58	2	1	3	50	-54
3	-5	3	17	-15	-5	-3	3	24	22	6	-2	3	37	-39	-6	0	3	53	-61	3	1	3	8	-7
4	-5	3	30	28	-4	-3	3	10	-8	8	-2	3	18	17	-5	0	3	20	-20	4	1	3	22	25
5	-5	3	55	55	-3	-3	3	42	-40	9	-2	3	23	22	-4	0	3	18	22	5	1	3	50	56
6	-5	3	47	47	-2	-3	3	60	-57	10	-2	3	25	23	-3	0	3	58	71	6	1	3	43	47
7	-5	3	29	28	-1	-3	3	50	-49	11	-2	3	18	16	-2	0	3	66	78	7	1	3	20	23
9	-5	3	33	-31	0	-3	3	7	-8	-13	-1	3	17	-13	-1	0	3	49	48	9	1	3	25	-23
10	-5	3	42	-40	1	-3	3	29	26	-11	-1	3	21	25	0	0	3	9	11	10	1	3	33	-33
-11	-4	3	11	-9	2	-3	3	50	46	-10	-1	3	34	37	1	0	3	45	-52	11	1	3	22	-19
-10	-4	3	24	-24	3	-3	3	54	52	-9	-1	3	33	34	2	0	3	70	-82	-13	2	3	23	20
-9	-4	3	46	-45	4	-3	3	36	35	-8	-1	3	10	10	3	0	3	54	-63	-12	2	3	16	15
-8	-4	3	29	-29	5	-3	3	21	-20	-7	-1	3	21	-22	4	0	3	21	-22	-11	2	3	17	-17
-7	-4	3	9	7	6	-3	3	27	-26	-6	-1	3	52	-56	5	0	3	16	17	-10	2	3	31	-31
-6	-4	3	42	39	7	-3	3	25	-26	-5	-1	3	60	-63	6	0	3	37	41	-9	2	3	45	-48
-5	-4	3	56	51	8	-3	3	33	-33	-4	-1	3	36	-36	7	0	3	48	52	-8	2	3	34	-37
-4	-4	3	64	57	9	-3	3	20	-22	-2	-1	3	59	57	8	0	3	32	32	-7	2	3	18	16
-3	-4	3	12	10	10	-3	3	20	19	-1	-1	3	74	73	10	0	3	19	-18	-6	2	3	49	48
-2	-4	3	31	-31	11	-3	3	30	29	0	-1	3	64	62	11	0	3	30	-30	-5	2	3	55	52
-1	-4	3	57	-55	-13	-2	3	18	-16	1	-1	3	12	13	-14	1	3	16	11	-4	2	3	43	41
0	-4	3	60	-58	-12	-2	3	19	-18	2	-1	3	23	-25	-13	1	3	29	25	-3	2	3	17	15
1	-4	3	40	-38	-10	-2	3	13	9	3	-1	3	35	-38	-12	1	3	33	30	-2	2	3	28	-25
3	-4	3	43	40	-9	-2	3	35	35	4	-1	3	60	-66	-11	1	3	21	21	-1	2	3	58	-53
4	-4	3	58	57	-8	-2	3	41	43	5	-1	3	44	-47	-10	1	3	8	-9	0	2	3	57	-54
5	-4	3	40	38	-7	-2	3	25	26	7	-1	3	30	33	-9	1	3	32	-33	1	2	3	36	-36
6	-4	3	12	12	-5	-2	3	38	-38	8	-1	3	39	41	-8	1	3	54	-59	3	2	3	34	34
7	-4	3	19	-18	-4	-2	3	54	-52	9	-1	3	31	32	-7	1	3	29	-33	4	2	3	49	49
8	-4	3	38	-36	-3	-2	3	62	-59	10	-1	3	16	16	-6	1	3	8	-7	5	2	3	39	44
9	-4	3	38	-37	-2	-2	3	26	-25	11	-1	3	12	-9	-5	1	3	18	19	6	2	3	9	3
10	-4	3	11	-7	-1	-2	3	25	23	12	-1	3	19	-18	-4	1	3	48	53	7	2	3	17	-15
-12	-3	3	21	-21	0	-2	3	58	55	-13	0	3	13	11	-3	1	3	81	86	8	2	3	27	-27
-11	-3	3	25	-25	1	-2	3	74	69	-12	0	3	28	28	-2	1	3	37	36	9	2	3	28	-27
-10	-3	3	15	-16	2	-2	3	44	42	-11	0	3	40	38	-1	1	3	17	-15	10	2	3	17	-16
-8	-3	3	21	19	3	-2	3	12	11	-10	0	3	23	23	0	1	3	59	-58	-13	3	3	9	-10
-7	-3	3	41	38	4	-2	3	38	-40	-8	0	3	31	-33	1	1	3	68	-70	-12	3	3	23	-22

TABLE 39 (CONTINUED)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-11	3	3	22	-20	2	4	3	26	21	-4	6	3	19	19	-1	8	3	26	-25	1	-5	4	42	41
-10	3	3	11	-7	4	4	3	14	-12	-3	6	3	42	40	0	8	3	29	-27	2	-5	4	46	44
-9	3	3	24	-27	5	4	3	43	-44	-2	6	3	48	44	1	8	3	20	-19	3	-5	4	26	24
-8	3	3	15	11	6	4	3	22	-20	-1	6	3	48	49	3	8	3	22	23	5	-5	4	31	-30
-7	3	3	46	44	8	4	3	8	4	1	6	3	46	-46	4	8	3	22	21	6	-5	4	36	-35
-6	3	3	52	48	9	4	3	12	11	2	6	3	46	-45	5	8	3	19	19	-8	-4	4	30	26
-5	3	3	27	24	10	4	3	18	17	3	6	3	22	-18	-8	9	3	12	10	-6	-4	4	10	-11
-3	3	3	40	-37	-13	5	3	11	-11	4	6	3	15	-13	-7	9	3	23	21	-5	-4	4	38	-36
-2	3	3	57	-54	-11	5	3	23	23	6	6	3	23	21	-6	9	3	21	19	-4	-4	4	56	-53
-1	3	3	47	-46	-10	5	3	30	26	7	6	3	27	27	-5	9	3	18	14	-3	-4	4	34	-33
0	3	3	11	-12	-9	5	3	30	26	8	6	3	17	16	-3	9	3	20	-20	-2	-4	4	31	26
1	3	3	20	17	-8	5	3	15	12	-11	7	3	17	13	-2	9	3	26	-26	-1	-4	4	37	35
2	3	3	51	52	-7	5	3	17	-14	-9	7	3	26	-24	-1	9	3	18	-18	0	-4	4	42	41
3	3	3	37	32	-6	5	3	44	-40	-8	7	3	38	-33	1	9	3	11	8	1	-4	4	35	34
4	3	3	30	31	-5	5	3	47	-43	-7	7	3	29	-26	2	9	3	20	21	2	-4	4	10	13
5	3	3	9	-10	-4	5	3	36	-34	-5	7	3	23	21	-1	-7	4	19	-19	3	-4	4	20	-19
6	3	3	22	-23	-2	5	3	29	27	-4	7	3	41	40	0	-7	4	31	-31	4	-4	4	36	-36
7	3	3	28	-28	-1	5	3	50	47	-3	7	3	32	29	1	-7	4	28	-28	5	-4	4	38	-38
8	3	3	25	-24	0	5	3	41	37	-2	7	3	17	17	2	-7	4	11	-10	6	-4	4	21	-21
10	3	3	12	14	1	5	3	20	20	-1	7	3	9	1	-5	-6	4	24	22	-9	-3	4	23	22
-13	4	3	23	-19	3	5	3	24	-21	0	7	3	27	-24	-3	-6	4	18	-17	-7	-3	4	27	-27
-12	4	3	32	-33	4	5	3	44	-46	1	7	3	46	-41	-2	-6	4	35	-34	-6	-3	4	33	-31
-11	4	3	10	-9	5	5	3	32	-33	2	7	3	34	-36	-1	-6	4	28	-26	-5	-3	4	27	-27
-10	4	3	19	19	7	5	3	21	19	4	7	3	18	17	0	-6	4	27	-26	-4	-3	4	26	-24
-9	4	3	29	28	8	5	3	25	24	5	7	3	27	25	2	-6	4	34	33	-2	-3	4	42	40
-8	4	3	39	36	9	5	3	18	18	6	7	3	26	24	3	-6	4	33	35	-1	-3	4	54	51
-7	4	3	30	27	-12	6	3	22	18	7	7	3	9	12	4	-6	4	16	18	0	-3	4	38	37
-5	4	3	32	-31	-11	6	3	33	31	-10	8	3	25	-22	5	-6	4	9	8	2	-3	4	27	-26
-4	4	3	50	-48	-10	6	3	22	21	-9	8	3	25	-21	-7	-5	4	30	27	3	-3	4	41	-42
-3	4	3	43	-41	-9	6	3	9	-3	-8	8	3	18	-17	-6	-5	4	17	15	4	-3	4	38	-38
-2	4	3	23	-22	-8	6	3	26	-23	-6	8	3	25	20	-4	-5	4	27	-27	5	-3	4	12	-15
-1	4	3	12	8	-7	6	3	47	-40	-5	8	3	40	38	-3	-5	4	45	-43	6	-3	4	12	11
0	4	3	48	45	-6	6	3	43	-40	-4	8	3	31	30	-2	-5	4	27	-25	7	-3	4	23	23
1	4	3	51	50	-5	6	3	20	-18	-2	8	3	21	-18	0	-5	4	12	11	8	-3	4	31	31

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-10	-2	4	12	15	5	-1	4	27	33	0	1	4	18	19	-3	3	4	11	8	-6	5	4	10	7
-8	-2	4	32	-33	6	-1	4	13	11	1	1	4	34	37	-2	3	4	43	41	-5	5	4	24	22
-7	-2	4	37	-38	-11	0	4	15	-17	2	1	4	26	30	-1	3	4	39	38	-4	5	4	27	26
-6	-2	4	26	-26	-10	0	4	19	-20	3	1	4	17	20	0	3	4	25	24	-3	5	4	24	23
-4	-2	4	24	22	-9	0	4	15	-14	5	1	4	19	-21	2	3	4	23	-23	-1	5	4	17	-13
-3	-2	4	47	45	-7	0	4	19	24	6	1	4	29	-34	3	3	4	32	-33	0	5	4	26	-26
-2	-2	4	39	38	-6	0	4	26	32	7	1	4	21	-23	4	3	4	24	-24	1	5	4	24	-22
-1	-2	4	17	17	-5	0	4	22	28	-10	2	4	22	22	5	3	4	14	-15	2	5	4	11	-12
0	-2	4	10	-9	-3	0	4	11	-11	-9	2	4	26	24	6	3	4	10	12	4	5	4	9	13
1	-2	4	33	-31	-2	0	4	36	-40	-8	2	4	26	28	7	3	4	18	18	5	5	4	23	23
2	-2	4	43	-42	-1	0	4	40	-38	-6	2	4	15	-18	-10	4	4	12	8	-7	6	4	13	13
3	-2	4	26	-27	0	0	4	20	-23	-5	2	4	35	-37	-8	4	4	30	-28	-6	6	4	24	23
5	-2	4	21	22	2	0	4	21	27	-4	2	4	39	-38	-7	4	4	36	-34	-5	6	4	22	20
6	-2	4	25	26	3	0	4	30	35	-3	2	4	22	-24	-6	4	4	17	-15	-3	6	4	14	-10
7	-2	4	23	25	4	0	4	26	33	-1	2	4	31	29	-4	4	4	17	16	-2	6	4	22	-18
8	-2	4	11	12	5	0	4	9	6	0	2	4	43	41	-3	4	4	30	27	-1	6	4	26	-24
-10	-1	4	11	-13	6	0	4	16	-17	1	2	4	37	38	-2	4	4	31	27	0	6	4	17	-17
-9	-1	4	21	-20	7	0	4	19	-21	3	2	4	18	-21	-1	4	4	18	15	2	6	4	17	14
-8	-1	4	23	-25	8	0	4	14	-16	4	2	4	27	-28	0	4	4	10	-7	3	6	4	16	14
-7	-1	4	13	-13	-11	1	4	15	-16	5	2	4	27	-29	1	4	4	24	-22	-6	7	4	12	12
-5	-1	4	29	32	-9	1	4	12	15	6	2	4	16	-18	2	4	4	30	-29	-5	7	4	10	-8
-4	-1	4	30	33	-8	1	4	25	27	-10	3	4	25	25	3	4	4	19	-16	-4	7	4	17	-15
-3	-1	4	24	27	-7	1	4	28	31	-9	3	4	17	17	5	4	4	15	14	-3	7	4	24	-24
-1	-1	4	25	-24	-6	1	4	14	16	-7	3	4	28	-27	6	4	4	21	22	-2	7	4	17	-16
0	-1	4	37	-36	-4	1	4	27	-30	-6	3	4	27	-25	-9	5	4	15	-9	1	7	4	16	15
1	-1	4	32	-33	-3	1	4	38	-40	-5	3	4	31	-29	-8	5	4	32	-30	-2	0	5	10	10
2	-1	4	15	-16	-2	1	4	35	-36	-4	3	4	21	-22	-7	5	4	16	-15	-1	0	5	23	22
4	-1	4	22	28																				

TABLE 41 : FRACTIONAL COORDINATES (× 10^3) OF THE HYDROGEN ATOMS FOR (55) AND (58)[a]

	Compound (55)			Compound (58)		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
H(N5)	522	404	160	117	-159	1110
H(2*A*)	-236	649	-83	-	-	-
H(3*A*)	-304	744	-164	-	-	-
H(4*A*)	-12	817	-184	-	-	-
H(5*A*)	380	794	-117	-	-	-
H(6*A*)	450	699	-40	-	-	-
H(2*B*)	-181	668	68	283	326	252
H(3*B*)	-484	737	104	407	427	-22
H(4*B*)	-691	700	212	542	326	-87
H(5*B*)	-577	602	287	556	128	133
H(6*B*)	-247	538	253	430	23	389
H(2*C*)	914	359	220	66	-297	1449
H(3*C*)	1110	292	326	97	-473	1768
H(4*C*)	1005	293	455	245	-543	1798
H(5*C*)	632	344	471	370	-438	1547
H(6*C*)	398	403	354	342	-260	1224
H(1*A*1)	-	-	-	14	329	167
H(1*A*2)	-	-	-	85	285	-87
H(1*A*3)	-	-	-	131	386	198

[a] Numbered according to the atom to which bonded.

TABLE 42: ISOTROPIC THERMAL MOTION PARAMETERS (Å × 10^3) OF THE NON-HYDROGEN ATOMS FOR (55) AND (58), WITH E.S.D.'S IN PARENTHESES

	Compound (55)	Compound (58)
Hg	*a*	*a*
S	*a*	*a*
N(1)	38(6)	42(3)
N(2)	49(6)	42(3)
C(3)	40(7)	41(4)
N(4)	44(6)	43(3)
N(5)	48(6)	46(4)
C(1*A*)	38(7)	57(5)
C(2*A*)	43(7)	-
C(3*A*)	58(8)	-
C(4*A*)	62(8)	-
C(5*A*)	65(9)	-
C(6*A*)	53(8)	-
C(1*B*)	35(6)	43(4)
C(2*B*)	48(7)	56(5)
C(3*B*)	64(9)	73(6)
C(4*B*)	67(9)	66(6)
C(5*B*)	63(8)	62(5)
C(6*B*)	60(8)	53(5)
C(1*C*)	44(7)	40(4)
C(2*C*)	64(9)	54(5)
C(3*C*)	78(10)	54(5)
C(4*C*)	87(11)	62(5)
C(5*C*)	78(10)	68(6)
C(6*C*)	60(8)	54(5)

[a] Anisotropic thermal parameters in the form
$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$ with
U_{ij} for Hg Å^2 × 10^4 and U_{ij} for S Å × 10^3:

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(55)	Hg	475(7)	456(7)	471(7)	25(7)	76(5)	78(7)
	S	47(4)	51(5)	46(4)	11(4)	16(4)	2(4)
(58)	Hg	617(5)	391(4)	532(5)	117(3)	59(3)	120(3)
	S	52(3)	51(3)	68(3)	13(2)	14(2)	24(2)

the final atomic positional and thermal parameters are set out in Tables 40, 41, and 42. All computations were executed using the same programmes as described previously (Chapters II and III).

Molecular structure

The molecular structure of (55) with atomic nomenclature is shown in Figure 29; in (58) a methyl group replaces phenyl ring *A*. Bond lengths and angles for (55) and (58) are given in Figures 30 and 31 respectively for two molecules which relate to each other by a centre of symmetry. Tables 43 and 44 list the bond lengths and angles. Both crystals consist of discrete molecules, each containing a dithizone residue acting as a bidentate ligand coordinating through S and N. One phenyl group (*B*) of the ligand is attached to the chelate ring whereas the other phenyl group (*C*) is extended as far as possible from the central Hg atom with two intervening N atoms that hold it in the *trans*-configuration. The coordination geometries of (55) and (58) are illustrated in Figure 32. In each compound the Hg atom exhibits planar, irregular three-coordination, the geometry at the Hg atom being approximately T-shaped.

Mercury coordination

The Hg-C distances of 2.12(2) (55) and 2.06(1) Å (58) appear normal [*cf.* 2.10 Å in the adducts of diphenylmercury with methylated phenanthrolines[207] and 2.06(2) Å in gaseous CH_3HgCl[208]], while Grdenić[209] has remarked on the longer Hg-C bonds in aryl- compared with alkylmercury(II) derivatives. The Hg-S bond lengths [(55), 2.372(7); (58), 2.389(4) Å] do not depart from accepted values and it appears from recent tabulations[210,211] that all reliable Hg-S distances in truly two-coordinate mercury compounds lie

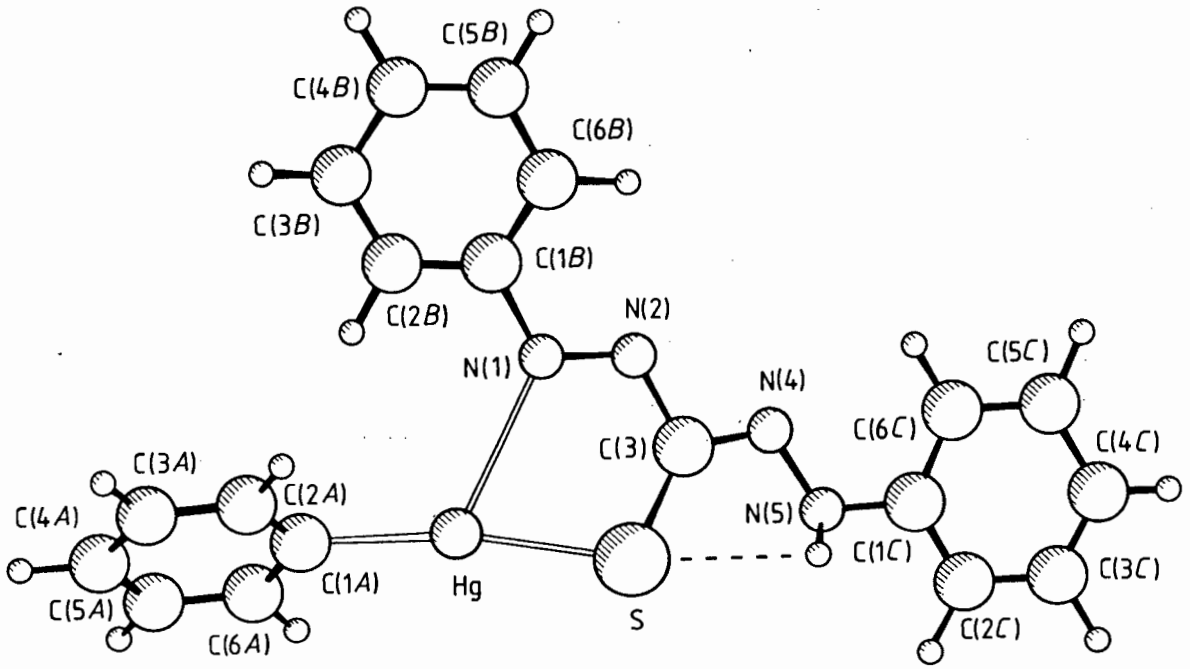


FIGURE 29 : Perspective view of the molecular structure of PhHg(HDz) (55) with atomic nomenclature; in MeHg(HDz) (58) a methyl group replaces phenyl ring *A*. The dashed line indicates a hydrogen bond.

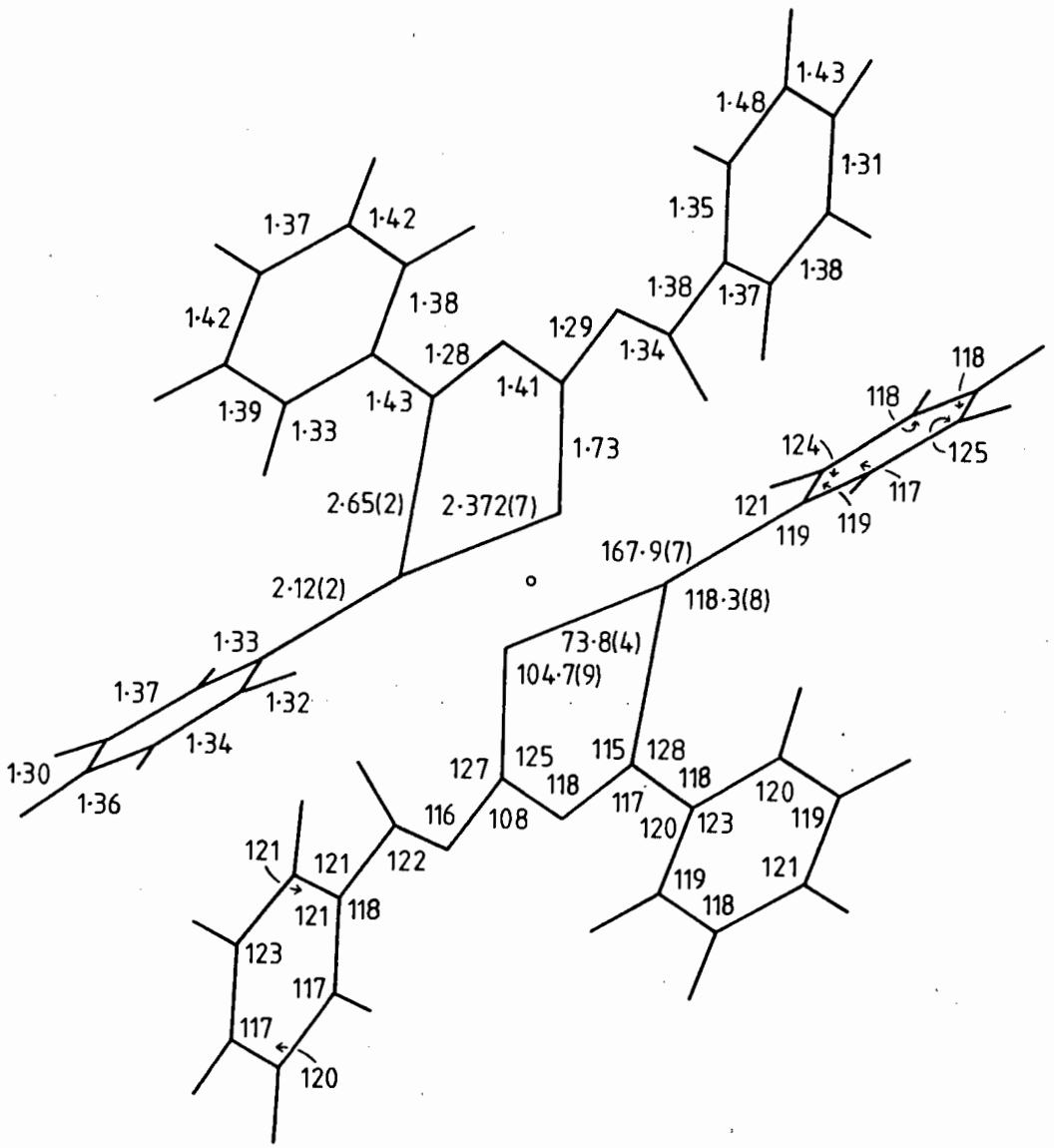


FIGURE 30 : Two molecules of PhHg(HDz) (55) related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s not shown are 0.03 - 0.04 for C-C and 0.03 Å for C-N, C-S, and N-N), while the lower molecule gives the bond angles (°; e.s.d.'s not shown are 2 - 4°).

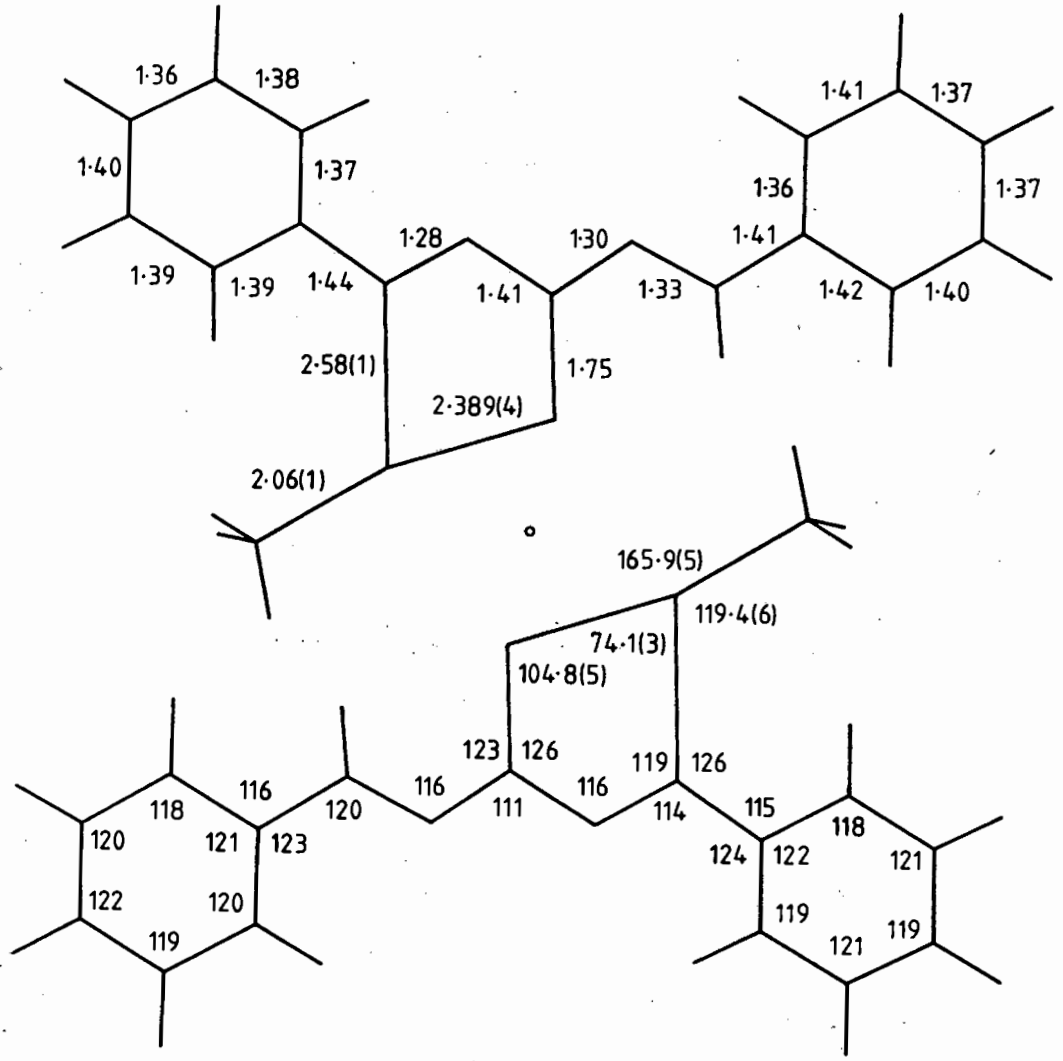


FIGURE 31 : Two molecules of MeHg(HDz) (58) related by a centre of inversion. The upper molecule shows bond lengths (Å; e.s.d.'s not shown are 0.02 - 0.03 for C-C and 0.02 Å for C-N, C-S, and N-N), while the lower molecule gives the bond angles (°; e.s.d.'s not shown are 1 - 2°).

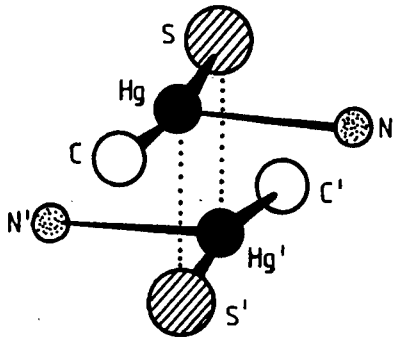


FIGURE 32 : The coordination spheres of the Hg atoms in molecules of PhHg(HDz) (55) and MeHg(HDz) (58) related by a centre of inversion. The closest interaction (dotted line) is Hg···S' [3.69(2) Å (55); 3.58(2) Å (58)].

within the narrow range 2.32 - 2.42 Å. Thus a strong covalent Hg-S bond is found in both PhHg(HDz) and MeHg(HDz) which may be compared with the Hg-S distance of 2.33(1) Å in $Hg(HDz)_2$ (5).[43] These Hg-S distances, which increase in the order (5) < (55) < (58), correspond with the decreasing Lewis acidity of the cations: Hg^{2+} > $PhHg^+$ > $MeHg^+$. The Hg-N distances of 2.65(2) (55) and 2.58(1) Å (58) are respectively 0.50 and 0.57 Å shorter than the sum (3.15 Å) of the van der Waals radii according to Bondi [r(Hg) 1.55, r(S) 1.80, r(N) 1.60, r(C) 1.77, r(H) 1.17 Å][126] and thus constitute weak bonds. They may be compared with the Hg-N distances found in mercury(II) complexes of 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) with higher coordination numbers for mercury, *e.g.*, 2.24(3) and 2.43(3) Å in $[CH_3Hg(bpy)]NO_3$ (irregular three-coordination),[212] 2.373(9) and 2.399(8) Å in $[HgBr_2(bpy)]_2$ (five-coordinate),[213] 2.42(2) - 2.52(2) Å in $[Hg(SCN)_2(phen)_2]$ (six-doordinate),[214] and 2.56(4) Å in $Hg(HDz)_2$ (5) (four-coordinate).[43] Covalent Hg-N distances are usually ~2.1 Å.[209] It was anticipated that the Hg-N(1) distance of 2.65(2) Å in PhHg(HDz) would be considerably shortened in MeHg(HDz), where there is no phenyl group (*A*) attached to Hg to hinder close approach of N(1) to Hg. That the Hg-N(1) distance in MeHg(HDz) [2.58(1) Å] is not substantially shorter illustrates the characteristically very weak residual Lewis acidity of the near-linear R-Hg-S unit. However, the C-Hg-S angle does decrease from 167.9(7)° in PhHg(HDz) to 165.9(5)° in MeHg(HDz), reflecting slightly decreased tendency for Hg 6*s*-orbital character to be concentrated in the Hg-C and Hg-S bonds. The concomitant increase in the Hg-S bond length in MeHg(HDz) was pointed out above.

Apart from the primary three-coordination there is a weak secondary interaction between the Hg atom in the reference molecule at x, y, z and the

towards additional donor atoms.[209,212] The coordination geometry now found in PhHg(HDz) and MeHg(HDz) implies that it is possible that chloromercury(II) dithizonate, HgCl(HDz), which also exhibits photochromic properties in organic solvents, exists as a monomer with a near-linear Cl-Hg-S system rather than as a chlorine bridged dimer.[43,206]

The dithizone residue

The calculated bond lengths in the dithizone residue (Figures 30 and 31) reveal a marked delocalization of π-electrons within the N-N-C-N-N chain and with the phenyl rings. While the formal double bonds C(3)=N(4) [(55), 1.29; (58), 1.30 Å] and N(1)=N(2) [(55), (58), 1.28 Å] are clearly extended in comparison with isolated double bonds, the formal single bonds N(2)-C(3) [(55), (58), 1.41 Å] and N(4) - N(5) [(55), 1.34; (58), 1.33 Å] are noticeably shortened. The S-C(3) lengths [(55), 1.73; (58), 1.75 Å] are of the expected magnitude and show that the electron delocalization found in the Ph-N-N-C-N-N-Ph chain does not discernibly extend to the S atom and that the S-C(3) bond order is ~1.0 in both compounds.[10] The S-C(3) bond order is probably decreased by donation of electron density to the Hg acceptor upon coordination, for the S-C bond order in crystalline dithizone itself is given as 1.2.[10] Calculated bond distances and angles relating to the phenyl groups are generally satisfactory in spite of one or two dubious C-C distances in PhHg(HDz); the mean C-C distance in the three phenyl rings of PhHg(HDz) is 1.37(5) Å and in the two phenyl rings of MeHg(HDz) is 1.39(2) Å.

A list of selected torsion angles and the parameters for several least-squares planes are given in Tables 45 and 46, respectively. From the chelate ring torsion angles it can be seen that in (55) the chelate ring is

TABLE 45 : SELECTED TORSION ANGLES (°)[a] FOR (55) AND (58)

	(55)	(58)
Hg-C(1A)-C(2A)-C(3A)	-178[b]	-
Hg-C(1A)-C(6A)-C(5A)	180	-
C(2A)-C(1A)-Hg-N(1)	-61	-
C(2A)-C(1A)-Hg-S	126	-
C(6A)-C(1A)-Hg-N(1)	125	-
C(6A)-C(1A)-Hg-S	-48	-
N(1)-C(1B)-C(2B)-C(3B)	-179	-178[b]
N(1)-C(1B)-C(6B)-C(5B)	-177	180
C(2B)-C(1B)-N(1)-N(2)	168	-162
C(2B)-C(1B)-N(1)-Hg	-6	23
C(6B)-C(1B)-N(1)-N(2)	-12	20
C(6B)-C(1B)-N(1)-Hg	174	-156
N(5)-C(1C)-C(2C)-C(3C)	-178	180
N(5)-C(1C)-C(6C)-C(5C)	180	180
C(2C)-C(1C)-N(5)-N(4)	-173	-179
C(6C)-C(1C)-N(5)-N(4)	6	1
N(4)-C(3)-N(2)-N(1)	169	-177
S-C(3)-N(2)-N(1)	-11	2
N(2)-C(3)-N(4)-N(5)	-174	179
S-C(3)-N(4)-N(5)	5	0
N(2)-C(3)-S-Hg	21	0
N(4)-C(3)-S-Hg	-158	180
C(1B)-N(1)-N(2)-C(3)	180	180
Hg-N(1)-N(2)-C(3)	-6	-4
C(1B)-N(1)-Hg-C(1A)	9	-6
C(1B)-N(1)-Hg-S	-172	178
N(2)-N(1)-Hg-C(1A)	-165	179
N(2)-N(1)-Hg-S	14	3
C(3)-N(4)-N(5)-C(1C)	175	175
C(3)-S-Hg-C(1A)	159	-166
C(3)-S-Hg-N(1)	-14	-2

[a] The torsion angle convention is that of Klyne and Prelog[124] and was defined in Table 12 (Chapter II). Phenyl-ring torsion angles are all < 7° (55) or < 2° (58) and are omitted.

[b] Estimated standard deviations are *ca.* 1°

TABLE 46 : LEAST-SQUARES PLANES PARAMETERS FOR PHENYLMERCURY(II) DITHIZONATE (58) AND METHYLMERCURY(II) DITHIZONATE (58)

(a) Equations of least-squares planes for (55) and (58) expressed in orthogonalized space as

$PI + QJ + RK = S$

Plane 1 : all non-hydrogen atoms

Compound (55) $0.5161I + 0.7043J + 0.4875K = 9.6413$

Compound (58) $0.2791I + 0.6064J + 0.7445K = 2.9128$

Plane 2 : chelate ring

Compound (55) $0.7200I + 0.5765J + 0.3863K = 7.6559$

Compound (58) $0.2286I + 0.6399J + 0.7337K = 2.7027$

Plane 3 : thiocarbazone chain

Compound (55) $0.6421I + 0.7396J + 0.1812K = 8.8509$

Compound (58) $0.2364I \quad 0.6397J + 0.7313K = 2.7292$

Plane 4 : phenyl ring *C*

Compound (55) $0.4950I + 0.8405J + 0.2204K = 9.4555$

Compound (58) $0.2898I + 0.5760J + 0.7644K = 3.2256$

Plane 5 : phenyl ring *B*

Compound (55) $0.6426I + 0.5380J + 0.5455K = 7.5175$

Compound (58) $0.4530I + 0.3583J + 0.8163K = 3.5963$

Plane 6 : phenyl ring *A*

Compound (55) $-0.1582I + 0.5183J + 0.8404K = 6.463$

Plane 7 : all non-hydrogen atoms excluding phenyl ring *A*

Compound (55) $0.6033I + 0.7542J + 0.2591K = 9.3953$

(Continued overleaf)

TABLE 46 (CONTINUED)

(b) Deviations (Å × 10^2) from planes for compounds (55) and, in parentheses, (58). Atoms included in the calculation are marked by asterisks. All e.s.d.'s are < 0.03 Å.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6	Plane 7
Hg	-57(-18)*	10 (-2)*	78 (-3)	123(-49)	-31 (-87)	-6	37*
S	-116(-8)*	-15 (1)*	-3 (-1)*	11(-30)	-40 (-21)	53	-45*
N(1)	-34(2)*	-11 (3)*	12 (3)*	80(-24)	-4 (-2)	189	-6*
N(2)	-36(2)*	2 (-2)*	-8 (-2)*	46(-19)	20 (34)	195	-25*
C(3)	-61(1)*	14 (0)*	-6 (-1)*	22(-18)	19 (32)	94	-32*
N(4)	-35(8)*	49 (0)	-5 (-1)*	12 (-6)	68 (75)	131	-27*
N(5)	-42(9)*	77 (4)	10 (2)*	2 (-3)	85 (79)	52	-20*
C(1A)	-8(-16)*	39 (9)	161 (7)	225(-55)	-23(-142)	2*	115
C(2A)	-75*	-53	91	175	-112	-1*	48
C(3A)	-42*	-32	147	243	-105	0*	101
C(4A)	48*	71	263	352	-19	0*	212
C(5A)	116*	163	334	403	72	2*	280
C(6A)	82*	141	278	335	63	-2*	227
C(1B)	-8(1)*	-22 (-1)	19 (0)	105(-26)	-1 (0)*	293	2*
C(2B)	18(40)*	-11 (43)	55 (44)	164 (7)	-2 (1)*	300	45*
C(3B)	44(39)*	-21 (40)	55 (42)	190 (5)	2 (0)*	400	55*
C(4B)	36(2)*	-49 (5)	1 (-2)	146 (30)	-1 (-1)*	487	12*
C(5B)	8(-33)*	-62(-46)	-47(-43)	84(-60)	-2 (1)*	477	-34*
C(6B)	-12(-36)*	-44(-46)	-38(-44)	66(-60)	2 (-1)*	379	-36*
C(1C)	-7(6)*	126 (-6)	23 (-7)	0 (-1)*	146 (115)	86	-5*
C(2C)	-2(5)*	166 (-4)	50 (-7)	2 (0)*	174 (114)	11	14*
C(3C)	28(0)*	210(-15)	59(-18)	-4 (1)*	231 (147)	41	26*
C(4C)	68(-5)*	230(-28)	54(-30)	2 (-1)*	274 (178)	150	33*
C(5C)	65(-1)*	190(-27)	26(-28)	0 (1)*	247 (182)	233	14*
C(6C)	24(4)*	135(-16)	9(-17)	-1 (0)*	179 (148)	197	-7*

(c) Selected angles (°) between normals to planes. All e.s.d.'s are < 3°.

	(55)	(58)		(55)	(58)
Planes 1 and 2	15	4	Planes 2 and 6	59	-
Planes 1 and 3	19	3	Planes 3 and 4	11	5
Planes 1 and 4	17	2	Planes 3 and 5	24	21
Planes 1 and 5	12	18	Planes 3 and 6	64	-
Planes 1 and 6	46	-	Planes 4 and 5	27	16
Planes 2 and 3	16	1	Planes 4 and 6	57	-
Planes 2 and 4	22	5	Planes 5 and 6	50	-
Planes 2 and 5	10	21	Planes 6 and 7	59	-

slightly buckled (the largest deviation from the least-squares plane defined by the chelate ring is 0.15(3) Å) whereas the chelate ring in (58) is more planar (largest deviation 0.03(3) Å). In each structure the whole ligand residue is quite closely coplanar, suggesting that the chelate ring and thiocarbazone chain are conjugated with phenyl rings *B* and *C*; the same conclusion was reached above in considering the thiocarbazone bond lengths. The dithizone residue in molecule (58) is actually more planar than in (55), and consideration of the bond lengths in the ligand residues (Figures 30 and 31) shows a consistent increase in single-bond character and decrease in double-bond character in the bond lengths of (58) compared with (55), although these bond length differences are within their e.s.d.'s. The largest deviation from the plane of the thiocarbazone chain [N-N-C(S)-N-N] is 0.12(3) (55) or 0.03(3) Å (58). In PhHg(HDz) the plane of phenyl ring *A* is twisted 59(3)° from the plane defined by the remainder of the molecule, thereby avoiding steric interaction with the phenyl ring (*B*) attached to the donor nitrogen. That the latter ring does not twist out of the plane is ascribed to the extensive electron delocalisation throughout the dithizone residue, as evidenced by the bond lengths found in the Ph-N-N-C-N-N-Ph chain and the planarity discussed above.

In both structures the imino hydrogen atom H(N5) participates in a weak intramolecular hydrogen bond to S, effectively locking the dithizone residue in an *anti,s-trans* configuration. The H(N5)···S distances of 2.40(9) (55) and 2.43(8) Å (58) [for fixed N(5)-H(N5) lengths of 1.00(1) Å] are significantly less than the sum of the van der Waals radii, while the N(5)···S separations are 2.92(3) (55) and 2.86(2) Å (58). The H(N5)···S distances of 2.4 Å are the same as that found in xanthane hydride,[175]

where the H atoms were located approximately and the presence of an almost linear intermolecular N-H···S hydrogen bond reported, and the same as that found in 3-methylthio-1,5-di(*o*-tolyl)formazan (30) (reported in Chapter III of this work). Although the distances are favourable for a strong intramolecular hydrogen bond, the stereochemistry of the sp^2-hybridized N(5) does not allow linearity of the N(5)-H(N5)···S angle [(55), 112(8)°; (58), 109(5)°] and thus the hydrogen bond formed is considerably weakened. Hydrogen bonding is nevertheless favoured here by the fact that in the configuration adopted one of the lone pairs of electrons on S is oriented towards H(N5). The *anti,s-trans* configuration of the N-N-C-N-N chain adopted in these structures is the same as that found in crystals of the free ligand (1) itself,[10] as adopted by the *o*-tolyl homologue of *S*-methyldithizone (30) (reported in Chapter III), and as found in the metal complexes $Hg(HDz)_2$ (5),[42,43] $Zn(HDz)_2$,[231] $Ni(HDz)_2$,[232] $Ni(HDz)_2(bpy)$,[233] and $Cu(HDz)_2$.[234]

Molecular packing

Projections of the molecular packing of PhHg(HDz) and MeHg(HDz) are given in Figures 33 and 34. Crystals of PhHg(HDz) consist of single molecules with a weak Hg···S' interaction to the sulphur atom in a molecule which is related by a centre of symmetry, as discussed above. These dimeric groups may be considered as packing units. The only other noteworthy intermolecular contact is S···S' [3.48(3) Å], and while there are several other contacts slightly less than the sum of the van der Waals radii, it is not believed that any of these has any important influence on the structure. Molecules of MeHg(HDz) are separated by normal van der Waals contacts; the weak Hg···S' interaction was discussed above and

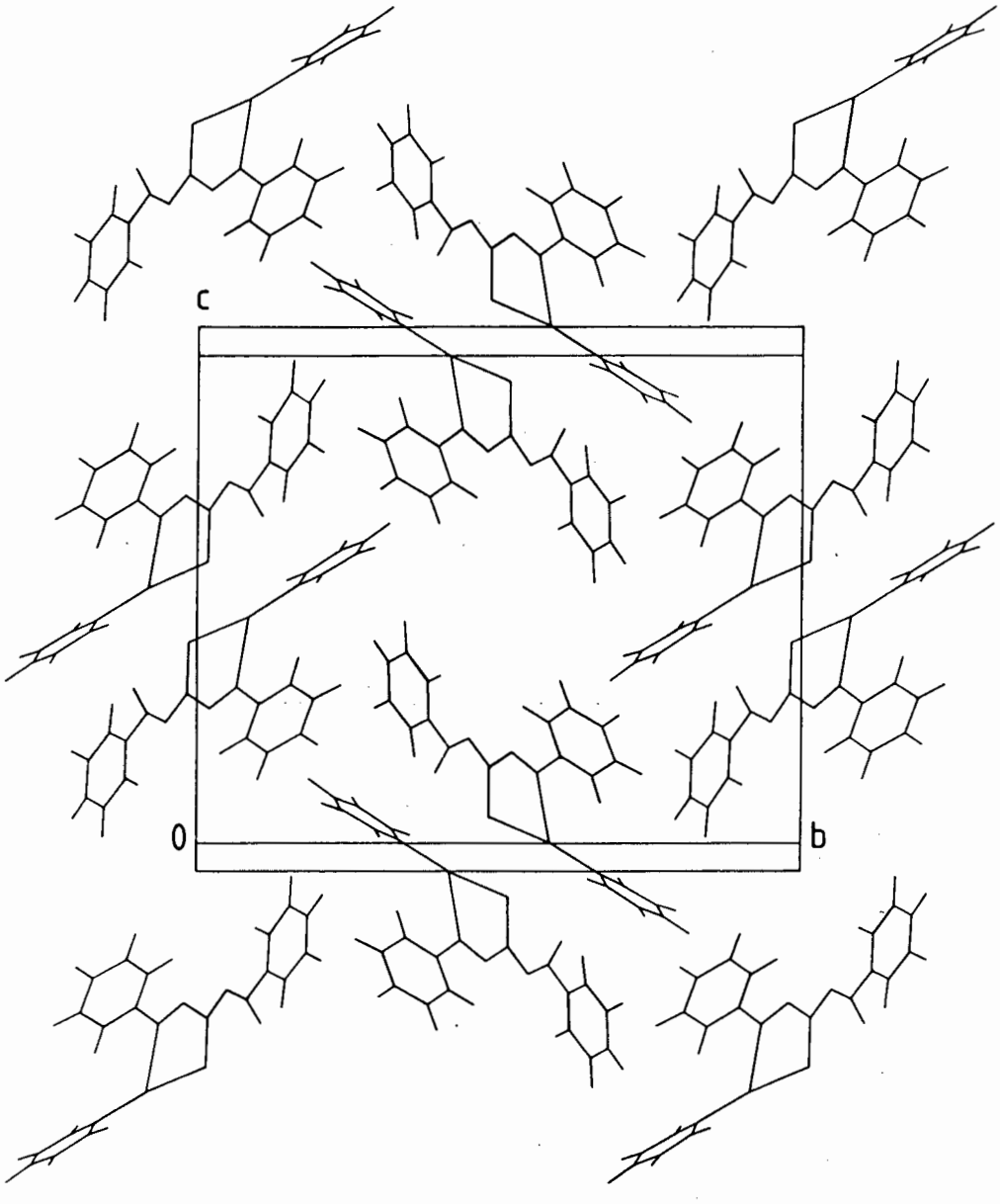


FIGURE 33 : The molecular packing in PhHg(HDz) (55) viewed down a^*.

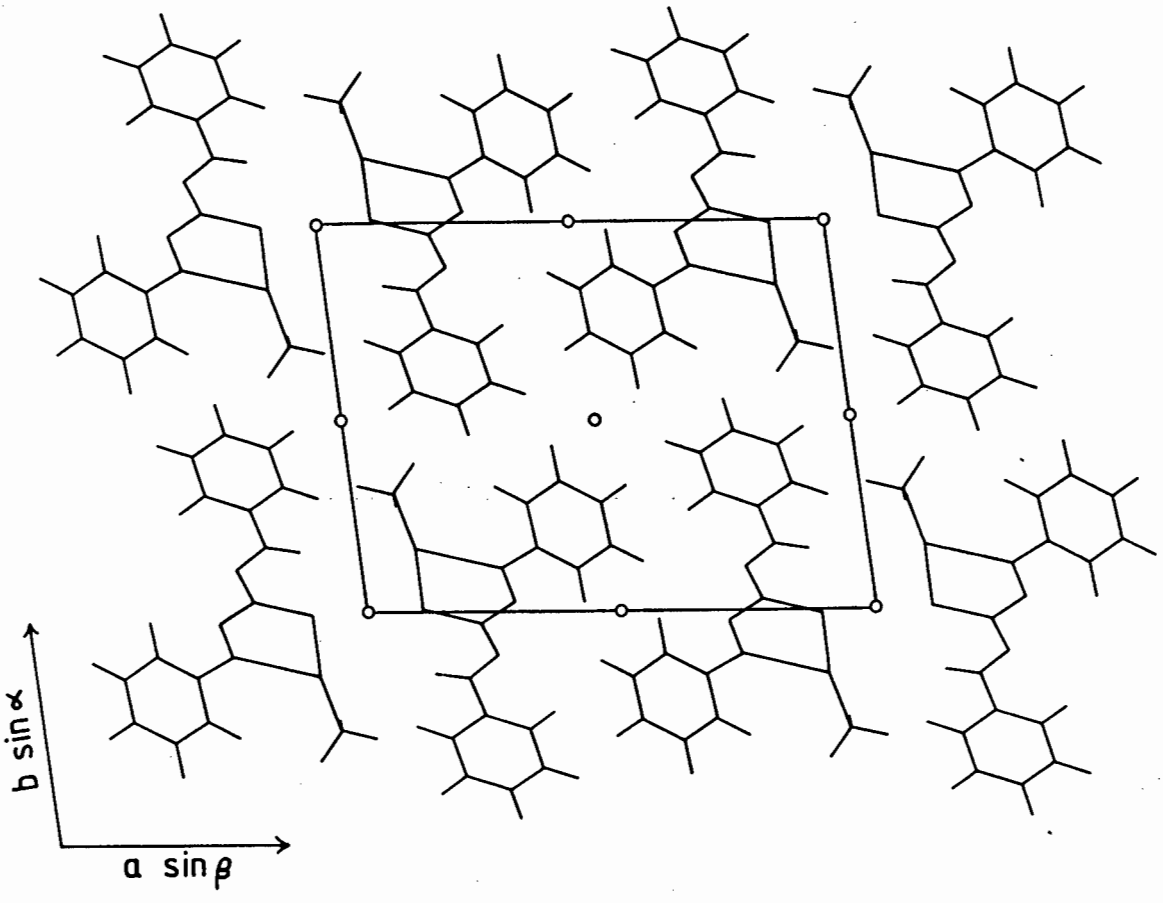


FIGURE 34 : The molecular packing in MeHg(HDz) (58) viewed down [001].

the dimeric groups may be considered as packing units. The molecules are stacked along *c*, their mean planes forming an angle of 51(1)° with the (001) plane.

3. Spectroscopic studies

Visible absorption, i.r., and ^1H n.m.r. spectroscopic data are given in Table 47 for the normal (yellow) and activated (blue) forms of the compounds studied. The organomercury(II) dithizonates show very similar spectral properties to the mercury(II) bis(dithizonate) (5), indicating that the dithizonate ligand is essentially unaffected by the substitution of an aryl or alkyl group for the second dithizonate 'on the other side' of the mercury(II) ion. The diffuse reflectance spectra of all the solids show a broad peak between 470 and 480 nm, while the normal yellow forms in chloroform solution exhibit absorption maxima from 470 to 485 nm. The i.r. spectra indicate that the normal yellow forms all possess a strongly hydrogen bonded NH group, which is known from the structural analysis reported in the previous Section of this Chapter to be hydrogen bonded to sulphur. The small shift in ν(N-H) (Table 47) on passing from the solid to solution indicates that this intramolecular N-H···S hydrogen bond is present in both the solid state and in solution. These facts indicate that the *X*-ray analyses of PhHg(HDz) (55) and MeHg(HDz) (58) reported in the previous Section, as well as the published structure of $Hg(HDz)_2$ (5)[42,43] determine the configuration of the ligand both in the solid and in solution.

There is a small hypsochromic shift in the visible spectra of the normal yellow organomercury(II) dithizonates when compared to the absorption of the bis-compound. This is hardly due to a structural difference but more likely is a reflection of electronic effects transmitted from one side of the mercury ion to the other. Thus PhHg(HDz) shows maximum absorbance at 470 nm while MeHg(HDz) absorbs at 480 nm; in (2,6-diMePh)-Hg(HDz), where a steric effect might be likely, the absorbance is

TABLE 47 : VISIBLE ABSORPTION, I.R., AND N.M.R. SPECTRAL DATA FOR NORMAL AND, IN PARENTHESES, ACTIVATED FORMS OF THE COMPOUNDS STUDIED

No.	Abbreviated name	Absorption maximum/nm		ν(N-H)/cm^{-1}		Chemical shift/ppm[a]		
		Solid[b]	$CHCl_3$ solution[c]	Solid[d]	CCl_4 solution	δ(NH)[e]	δ($ArCH_3$)	δ($HgCH_3$)
(5)	$Hg(HDz)_2$	480	485 (604) ε = 7050	3250	3275 (3344)	9.21 (10.52)	-	-
(55)	PhHg(HDz)	475	470 (609) ε = 3500	3253	3277 (3346)	9.19 (10.46)	-	-
(56)	(2,6-diMePh)Hg(HDz)	475	471 (608) ε = 4450	3256	3276 (3347)	9.20 (10.48)	2.44 (2.45)	-
(57)	(2,4,6-triMePh)Hg(HDz)	470	467 (610) ε = 4800	3252	3274 (3340)	9.19 (10.49)	2.33 (2.33) 2.39 (2.40)	-
(58)	MeHg(HDz)	480	480 (608) ε = 3800	3255	3277 (3344)	9.14 (10.46)	-	1.10 (1.26)
(59)	MeHg(*p*-tolyl-HDz)	477	479 (611) ε = 3950	3255	3276 (3344)	9.10 (10.45)	2.32 (2.32) 2.40 (2.40)	1.11 (1.25)
(60)	MeHg(*o*-tolyl-HDz)	477	480 (608) ε = 3750	3258	3280 (3346)	9.15 (10.42)	2.42 (2.42) 2.60 (2.60)	1.09 (1.23)

[a] 90 MHz ^1H n.m.r. spectra of $CDCl_3$ solutions at ambient temperature. Shifts are relative to TMS.

[b] Diffuse reflectance spectra; all broad peaks.

[c] ε/m^2 mol^{-1} given for normal form only.

[d] KBr pressed disks.

[e] Disappears on addition of D_2O.

virtually the same as in PhHg(HDz). On irradiation of solutions of $Hg(HDz)_2$ the colour changes to blue as the activated form $Hg(HDz^*)_2$ is produced (where the asterisk denotes the activated ring system), although there is no reason to suppose that Hg(HDz)(HDz*) is not formed, and in amounts that are dependent upon the intensity of illumination, the temperature, solvent, and so on. Since Hg(HDz*) is spectroscopically and kinetically indistinguishable from an equimolecular mixture of $Hg(HDz)_2$ and $Hg(HDz^*)_2$, one might assume that the photochromic process occurs in each ligand independently, and is unaffected by the presence of a second dithizonate residue attached to the central metal atom. The above evidence from the organomercury(II) compounds, however, suggests that the second dithizonate residue will perceive a somewhat different effect transmitted through the central mercury if the first residue is in the activated blue form. The present data do not allow prediction of whether this change will enhance or retard the rate of change of the second residue, however, and the effect is probably very small, if it exists at all. It is interesting to note that the extinction coefficient values for the absorption bands in the organomercury(II) complexes are virtually half of the value found for the bis-dithizonate, where, of course, there are two identical absorbing chromophores. The extinction coefficients for the blue forms were not obtained because of the difficulty of maintaining a steady state of 100% activated blue form, but estimates of 3900 $m^2\ mol^{-1}$ for $Hg(HDz)_2$ and 2200 $m^2\ mol^{-1}$ for the band due to the blue form in the organomercury dithizonates are not unreasonable.

The i.r. spectral shift of the ν(N-H) band produced by irradiation and consequent photo-isomerisation is from 66 to 71 cm^{-1} in the organomercuric

dithizonates and 69 cm^{-1} in $Hg(HDz)_2$, the shift being to higher wavenumber in both cases (Table 47). This indicates a weakening of the hydrogen bond in the blue forms and is consistent with the formation of an N-H···N hydrogen bond which is weaker because of the low basicity of the azo nitrogen. The difference in wavenumber is the same as that found for the two isomers of *S*-methyldithizone, (4), which was shown in Chapter III to exhibit *syn-anti* isomerism between forms containing N-H···N and N-H···S hydrogen bonds. It appears that in the mercury dithizonates the N-H···S hydrogen bond is broken on activation and *syn-anti* isomerism about the C(3)=N(4) bond is followed by rearrangement and the establishment of a new but weaker hydrogen bond between N(2) and N(5). Curtin and Hausser[235] have shown that such isomerism about azomethine groups can be very fast, whereas intermolecular proton transfer in dilute solution in aprotic and non-polar solvents has been found to be relatively slow,[236] and could be the rate-determining step. It may be assumed that no direct intramolecular hydrogen transfer from N(5) to N(2) occurs and it has been suggested[41] that a water molecule or a second molecule of complex or both must serve as a proton bridge, the activated complex for this reaction probably being a complex structure consisting of several water and dithizonate molecules bound together by hydrogen bonds. This hypothesis is supported by the dependence of the return rate on the concentration of water and complex, by the rapid deuterium exchange of the complex, and the observed pH and solvent sensitivity of the photochromic reaction.[40] The resulting activated structure (b) (Table 34) represents a drastically altered chromphore with a thiocarbonyl group: many organic compounds with this chromophore in a conjugated

system are known to be blue,[237] with visible bands in the same region (580 - 610 nm) as in the activated form of the mercury dithizonates.

The ^{1}H n.m.r. study of the organomercury(II) dithizonates was facilitated by their *ca.* 100-fold increase in solubility over that of the mercury(II) bis(dithizonate). Thus the spectra of the stable yellow forms of (58) - (60), all of which contain methylmercury, showed the methyl singlet at about δ 1.10 (Table 47). Irradiation by an intense beam of visible light using glass fibre optics (see Experimental Section) enabled the spectra of the blue photo-isomers to be recorded and a downfield shift of the $HgCH_3$ resonance by 0.16 ppm was observed, indicating a change in the character of the ligand donor atoms and pointing again to a thiocarbonyl group in the blue isomer. Transmittance of these electronic effects through the mercury atom was established by changing R in RHg(HDz) and monitoring the effect on the dithizonate chromophore, as mentioned above. The $J(^{199}Hg-^{1}H)$ coupling constant in CH_3HgX is known to vary considerably with the nature of X,[238] and although a $J(^{199}Hg-^{1}H)$ of 180.4 Hz was observed in the stable yellow form of MeHg(HDz), the ^{199}Hg satellite peaks were unfortunately not observed in the spectrum of the activated blue form due to a high noise level. It will be seen from Table 47 that on irradiation no new peaks were observed arising from any of the methyl groups attached to either the arylmercuric or dithizonate rings, and it is assumed that any changes were too small to be resolved. This seems reasonable considering the not dissimilar arrangement of the aryl rings in the yellow and proposed blue forms of the dithizonate residues in MeHg(*p*-tolyl-HDz) and MeHg(*o*-tolyl-HDz) (see Table 34),

while possibly the effect of the photo-isomerisation is not large enough to affect the shielding of the methyl groups on the arylmercuric rings in (2,6-diMePh)Hg(HDz) and (2,4,6-triMePh)Hg(HDz) to any marked extent. The formation of a different hydrogen bond in the activated form is clearly seen in the disappearance of the N*H* resonance at about δ 9.2 and its appearance at about δ 10.5 in the activated forms of all the complexes studied. A schematic representation of the changes found in the i.r. and ^{1}H n.m.r. spectra of MeHg(HDz) is given in Figure 35.

These results show that the organomercury(II) dithizonates (55) - (60) are photochromic in the same way as mercury(II) bis(dithizonate). Their visible, i.r. and ^{1}H n.m.r. spectra, when taken in conjunction with the crystallographically determined structures of the yellow forms, provide evidence in support of Meriwether's[41] proposed scheme for the photochromic reaction (5a) $\rightleftharpoons$ (5b) (Table 34), but final proof of the structure of the blue photo-isomer must await *X*-ray analysis of a suitable crystal. However, all attempts to isolate the blue solid failed in this work, and it seems very unlikely that the structure of the blue form will ultimately be proved crystallographically.

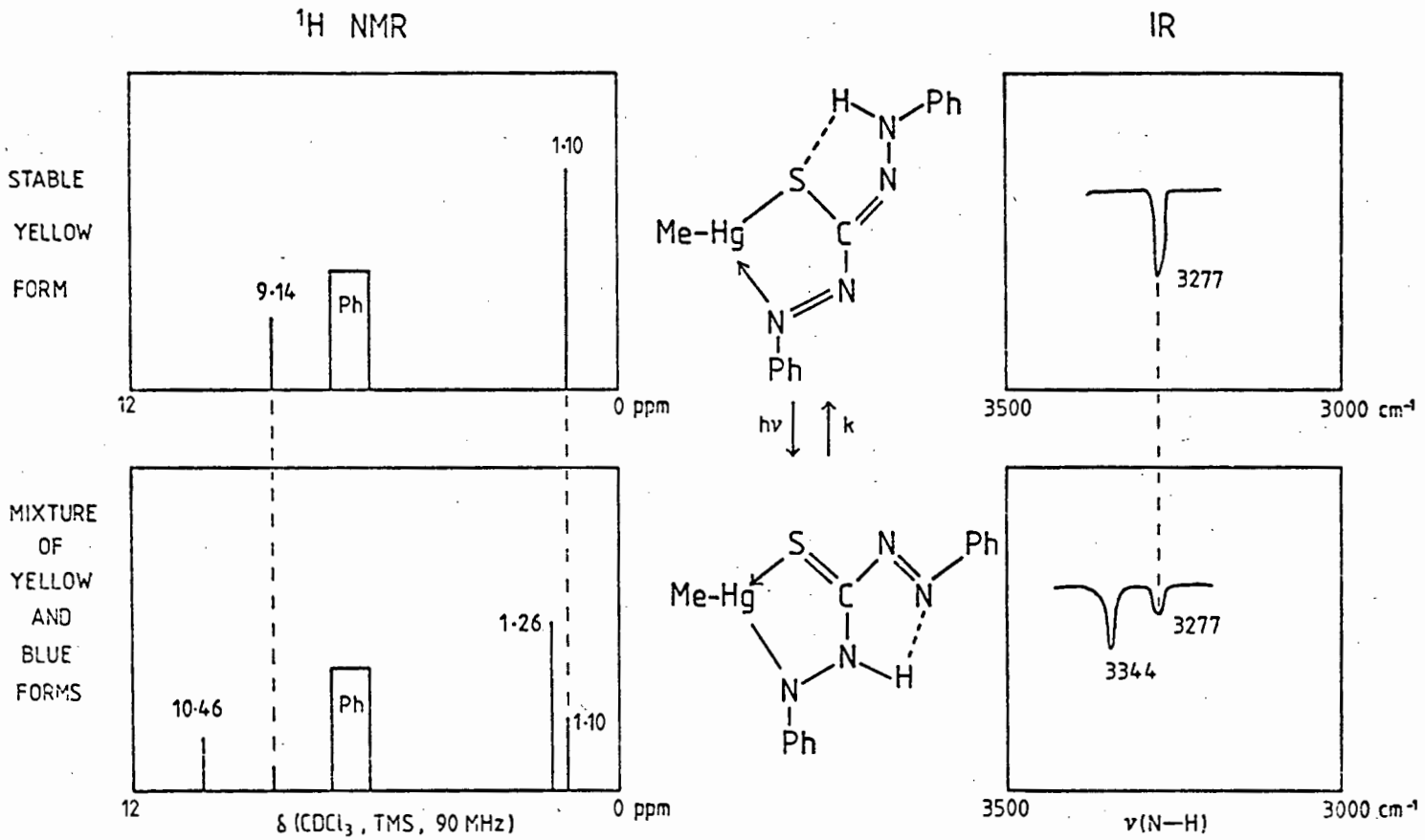


FIGURE 35 : Schematic representation of the changes in the i.r. and ^1H n.m.r. spectra of MeHg(HDz) (58) upon irradiation in chloroform solution.

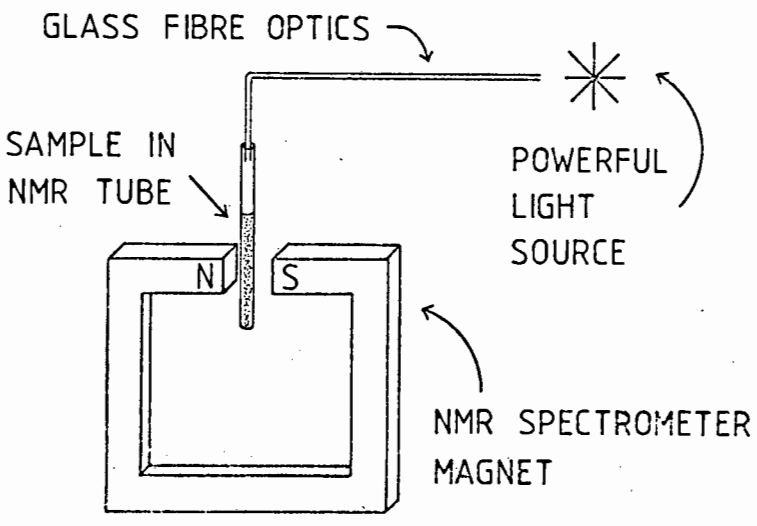
4. Experimental

General and spectroscopic

Visible absorption, diffuse reflectance, i.r., and n.m.r. spectra were generally measured on the same instruments and under the same conditions as the work reported in Chapter II. Special care was taken in cleaning the optical cells and n.m.r. tubes so as to remove traces of impurity which might accelerate the return reaction when trying to observe the activated blue form of the complexes. The cleaning was carried out as described in Chapter III. Chloroform, carbon tetrachloride, and deuterochloroform were scrupulously dried over molecular sieve and when required were withdrawn with a syringe from bottles fitted with rubber seals. The use of dry solvents ensures a sufficiently long half-life of the activated blue form ($t_{\frac{1}{2}}$ of the order of minutes) for spectroscopic measurements to be made.

The light source used in the visible absorption and i.r. experiments was a 500 W tungsten bulb housed in a standard manual 35 mm slide projector. Infrared radiation was absorbed by 2 cm of water in a glass cell. The visible spectra of the blue forms were recorded by irradiating the sample (*ca.* 10^{-5} *M*) in chloroform in a standard 1 cm quartz optical cell to produce the colour change and then scanning the region of interest at a rapid rate. Periodic scans then allowed the return reaction to be monitored (see Figure 28). Suitable i.r. spectra in the N-H stretching region were obtained in a similar fashion using *ca.* 10^{-2} *M* solutions in 1 cm silica optical cells. The ^{1}H n.m.r. spectra were obtained at 90 MHz on the Bruker WH-90DS spectrometer operating in the FT mode at ambient

temperature. Irradiation was achieved *in situ* by focusing a pencil-thin beam of light supplied by a Schott Mainz KL 150 B light source (150 W) into the open end of the n.m.r. tube positioned in the magnet using a glass-fibre optical system, as illustrated schematically below.



Preparations

General preparative procedures and facilities were unchanged from the work reported in Chapter II. The arylmercury(II) chlorides were synthesized by reported methods,[89,205] and these were reacted in stoicheiometric ratios with the appropriate thiocarbazone in a water/benzene extraction system. Estimates of the solubility of the organomercury(II) dithizonates were made by weighing the residue after evaporation of known volumes of filtered, saturated solutions. Results for the organomercury(II) dithizonates indicated that their saturated benzene solutions ranged

from 0.10 to 0.14 *M*, which is a 100-fold increase over the solubility of mercury(II) bis(dithizonate) in the same solvent.

Phenylmercury(II) chloride

Aniline (23.3 g; 0.25 mol) was mixed with concentrated hydrochloric acid (50 cm^3) and crushed ice (150 g) and diazotized at 0°C with a solution of sodium nitrite (17.5 g; 0.26 mol) in water (30 cm^3) in the usual fashion (see Chapter II). This phenyldiazonium chloride solution was then added to a mixture of mercury(II) chloride (68.0 g; 0.25 mol), copper(I) chloride (49.5 g; 0.25 mol), concentrated hydrochloric acid (50 cm^3), and crushed ice (150 g). The temperature was not allowed to exceed 5°C. The mixture expanded rapidly in volume and became frothy as nitrogen was evolved. Vigorous stirring was required while adding the diazonium solution, and then for a further 1 hour. The solid was filtered off, washed with water and then ethanol, dried over silica gel *in vacuo*, and then recrystallized from benzene to yield white satiny leaflets of phenylmercury(II) chloride [47.0 g, 60.0%; m.p. 249-251°C (lit.[89] 251°C)]. (Found : C, 23.05; H, 1.6%. Calc. for C_6H_5HgCl: C, 23.0; H, 1.6%.)

2,6-Dimethylphenylmercury(II) chloride

This was prepared from 2,6-dimethylaniline in exactly the same way as PhHgCl and was recrystallized from benzene to give white needles [47.1 g, 55.2%; m.p. 155-157°C (lit.[239] 156-157°C)] (Found: C, 28.1; H 2.6%. Calc. for C_8H_9HgCl: C, 28.2; H, 2.7%.)

2,4,6-Trimethylphenylmercury(II) chloride

This was also prepared in the same way as PhHgCl, starting from 2,4,6-trimethylaniline. Recrystallization from benzene give white needles [43.0 g, 48.4%; m.p. 197-199°C (lit.[240] 198-199°C)] (Found: C,30.1; H, 3.1%.)

Bis(1,5-diphenylthiocarbazonato-*N*,*S*)mercury(II) [(5); $Hg(HDz)_2$]

Solutions of mercury(II) chloride (0.54 g; 0.002 mol) in benzene (100 cm^3) and dithizone (1.02 g; 0.004 mol) in benzene (100 cm^3) were combined in a large separating funnel and shaken for 10 minutes with 1 *M* aqueous ammonia (200 cm^3). The bright red organic phase was washed with water, dilute aqueous ammonia (1*M*), and finally with water. The organic layer was separated, dried with sodium sulphate, and evaporated to dryness. Two recrystallizations from benzene-ethanol gave a dark red-brown microcrystalline product [0.98 g, 68.7%; m.p. 223-224°C decomp. (lit.[39] 225-226°C decomp.)]. (Found: C, 43.4; H, 3.0; N, 15.7%. Calc. for $C_{26}H_{22}N_8S_2Hg$: C, 43.9; H, 3.1; N, 15.8%.)

(1,5-Diphenylthiocarbazonato-*N*,*S*)phenylmercury(II) [(55); PhHg(HDz)]

This was prepared in the same way as the bis-compound (5), only using the phenylmercury(II) chloride synthesized as described above and half the quantity of ligand. Recrystallization from benzene-ethanol gave red-brown crystals [0.66 g; 62.0%; m.p. 172-173 °C decomp. (lit.[39] 174-175°C decomp.)]. (Found: C, 42.4; H, 3.1; N, 10.45%. Calc. for $C_{19}H_{16}N_4SHg$: C, 42.8; H, 3.0; N, 10.5%.)

(1,5-Diphenylthiocarbazonato-*N*,*S*)2,6-dimethylphenylmercury(II) (56)

This was prepared analogously to (55) above. Recrystallization from benzene-ethanol gave the red-brown product (0.82 g, 69.3%; m.p. 197-199°C decomp.). (Found: C, 46.5; H, 4.0; N, 9.2%. $C_{23}H_{24}N_4SHg$ requires C, 46.9; H, 4.1; N, 9.5%.)

(1,5-Diphenylthiocarbazonato-*N*,*S*)2,4,6-trimethylphenylmercury(II) (57)

This was prepared in an analogous fashion to (55) above. A red-brown powder was obtained after recrystallization from benzene-ethanol (0.69 g, 56.3%; m.p. 184-186°C decomp.). (Found: C, 48.2; H, 4.3; N, 9.1%. $C_{25}H_{28}N_4SHg$ requires C, 48.6; H, 4.6; N, 9.1%.)

(1,5-Diphenylthiocarbazonato-*N*,*S*)methylmercury(II) [(58); MeHg(HDz)]

This was prepared in the same way as the arylmercury(II) derivatives above, using methylmercury(II) acetate supplied by Ventron, Alfa Division. Recrystallization from benzene/n-hexane gave a red-brown microcrystalline powder (0.60 g, 64.2%; m.p. 152-155°C). (Found: C, 35.4; H, 2.9; N, 11.8%. $C_{14}H_{14}N_4SHg$ requires C, 35.7; H, 3.0; N, 11.9%.)

[1,5-Di(*p*-tolyl)thiocarbazonato-*N*,*S*]methylmercury(II) (59)

This was prepared in the same way as MeHg(HDz) (58) above using the 1,5-di(*p*-tolyl)thiocarbazone (45) synthesized for the work reported in Chapter IV, and was recrystallized from benzene/n-hexane to give the red-brown product (0.52 g, 52.1%; m.p. 149-151°C). (Found: C, 38.2; H, 3.5; N, 11.1%. $C_{16}H_{18}N_4SHg$ requires C, 38.5; H, 3.6; N, 11.2%.)

[1,5-Di(*o*-tolyl)thiocarbazonato-*N*,*S*]methylmercury(II) (60)

This was also synthesized in the same way as MeHg(HDz) (58) from 1,5-di(*o*-tolyl)thiocarbazone (Chapter IV). Recrystallization from benzene-ethanol gave a red-brown microcrystalline powder (0.61 g, 61.0%; m.p. 158-159°C). (Found: C, 38.3; H, 3.2; N, 11.0%. $C_{16}H_{18}N_4SHg$ requires C, 38.5; H, 3.6; N, 11.2%.)

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